Studies on Polyelectrolyte solutions(Dissertation_全文)

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CHAPTER 1

INTRODUCTION

The story of electrolytes begins in 1832,[1] when Faraday has discovered that the solutions of acids, bases and salts conduct an electric current and the amount of electricity is determined by the electrochemical equivalent of the atom or atom-group. This discovery, the Faraday law of electrolysis as we know now, suggests that the flow of electricity in solutions considered is related to new solute particles and led Helmholtz[2] to the assumption of "Atomender Elektrizität", inherent to the atom or atom-group. Before the production of the new solute particles became well-established, however, another evidence had to be accumulated. In 1887, van't Hoff[3] found an anomaly that the solutions conducting electricity do not obey the simple van't Hoff law, and introduced was the van't Hoff coefficient into his law. The conducting power of solutions for electricity and their abnormal thermodynamic behaviour were clearly unified by Arrhenius[4] who propounded a view that when an electrolyte is dissolved into water, the molecule dissociates into new particles, "ions" as Faraday had named originally, to a greater or less extent.

From 1887 afterwards the knowledge of ionic solution has enormously increased. The experimental results were in accord with the prediction of the Arrhenius dissociation theory for a group of electrolytes but this was not the case for

other: the conventional classification was set up into "weak" and "strong". We need only to mention here, as an example of outstanding deviation from the Arrhenius theory, the well-established $C^{1/2}$ rule (C, concentration of electrolyte), which was found to apply the thermodynamic data, for example osmotic coefficient, and also the transport phenomena of strong electrolyte solutions. It was made clear that failure of the Arrhenius theory comes from the omission of interionic interaction, which was easily recognised to be of Coulombic nature.

1923 was a starting point for introducing the new era in the history of electrolyte theory, when Debye and Hückel[5] succeeded in treating the interionic interaction. According to Arrhenius, the undissociated molecules are in equilibrium with the dissociated ions in a sense of Guldberg-Waage. Consequently, for weak electrolytes, which produce a relatively small amount of ions, only short-range force would be a dominant factor to be taken into consideration, whereas for strong electrolytes Coulombic interaction intervenes that can not be overlooked. Therefore, in strong electrolyte solutions there can be no random distribution of the ions. Such an understanding was first suggested by Milner[6] and succeeded to Debye. The latter assumed the Boltzmann distribution for ions, in contrast to Ghosh[7] who developed an erroneous theory based on a regular distribution. The success of the Debye-Hückel theory was so glittering in interpreting experimental data that

their equations form the basis of all the considerations which have been published on ionic interaction.

The Debye-Hückel theory has, of course, a limit of applicability which is not inconsistent to the assumptions made at the beginning: that the ion is a point-charge, and the electrostatic energy is much smaller than the kinetic one, and the molecule can dissociate into ions completely. Recent extensions proposed are related to these three. We will discuss, here, the outline of these extensions that are of importance in the field of polyelectrolyte solutions.

(A) Point-Charge Approximation. When we want to have theory that can explain the behaviour of concentrated solution, where the original Debye-Hückel theory clearly fails, we will notice that the exclusion volume of ions has to be taken into account. Debye and Hückel, in their second approximation, manipulated this effect, though not sufficiently, with the assumption that only the central ion has a finite size and all others are point-charges. The first approximation was somewhat improved by this subtle treatment, which was obliged to invoke by their adopting the Boltzmann distribution. According to this distribution, even an infinite number of ions may be present simultaneously in a volume element of the solution. However, this can never be possible: the ions can not approach within a distance to each other, that depends on the crystallographic radius and the state of hydration of the ions. Debye's

adoptation of the Boltzmann distribution, thus leads to an overestimation of the interionic interaction, as comparison between theory and experiment indicates: the error becomes greater with increasing concentration. In 1952, Wicke and Eigen[8] took one step towards extending the Debye-Hückel theory to higher concentration ranges in a different way from that of some other authors[9] who looked for the ways of circumventing the difficult problem of introducing the concentration effect. The novel idea developed by Wicke and Eigen is in attracting our attention to the distribution formula itself. The Boltzmann formula is replaced by one of a new type which is a special case of the equation derived by Falkenhagen.[10] The fairly good agreement with experiment is obtained by using a single parameter, ionic exclusion volume, in higher concentration ranges.

It must be mentioned that, with regards to the theory of irreversible process, great effort has been made to introduce an ion diameter with the aim of extending the Debye-Hückel-Onsager-Fuoss theory.[11]

(B) Small Electrostatic Potential Energy. This assumption can be expressed by the following relation

$$e\psi/kT \ll 1, \qquad (1\text{-}1)$$

where e is the charge, ψ the electrostatic potential, k the Boltzmann constant. This was a very important assumption

which led Debye and Hückel to the self-consistent solution of the Poisson-Boltzmann equation, though they did not notice the importance at all. Onsager and others[12] have extensively discussed the nature of this approximation and pointed out that it was more than a mere mathematical device to avoid complicated calculation. It is, however, evident that (1-1) restricts the application of the theory to dilute solutions of electrolytes of low valency. Gronwall et al.[13] took a view that this approximation had to be removed so as to obtain more reasonable agreement between theory and experiment than that by the Debye-Hückel theory. In fact the more exact solution of the non-linearised Poisson-Boltzmann equation was useful in interpreting some of the experimental results. However some authors[12] regarded this way of approach as logically doubtful because the treatment is not self-consistent.

It is worthy to notice that ψ in (1-1) does not denote the potential at a specified distance from the central ion. ψ decreases with increasing distance monotonically so that this assumption will be realised also for solutions of electrolytes of higher valency if the solutions are extremely dilute. However, on the contrary, even in the case of 1-1 type electrolytes, it will be inlegitimate in a vicinity of the ion when the ions have a small radius. Thus we see that the assumption should be interpreted to be for all important values of the distance.

The Wicke-Eigen theory, just discussed above, also assumes (1-1). With the results now available, it is possible to see that the assumption holds in more concentrated solutions. This is rather curious at a glance, but "all important values of the distance" should be interpreted to become larger with increasing exclusion volume of ions. If this consideration is justified, we would be able to stand in an optimistic view that the dilute solutions of polyelectrolytes, the volume exclusion effect of that is generally pronounced, may be understood with use of a similar method to that applied to the solutions of simple electrolytes.

We mentioned the inlegitimacy of (1-1) for small ions. This was a starting point of Bjerrum's treatemnt of ion-pair formation, which will be discussed later on.

(C) Complete Dissociation. A view that the molecule of strong electrolyte completely dissociates into ions in aqueous solution was first taken by Bjerrum[15] who observed that the optical properties of this solution did not depend on the concentration. The Debye-Hückel theory, formulated on the hypothesis of complete dissociation, won so general acceptance that " a great deal of time was spent in demolishing spurious degrees of dissociation arrived at by ignoring interionic interaction" as pointed out by Bell.[16] However, the pendulum began to swing back when Bjerrum[14] proposed the concept of ion-pairing. As mentioned above, Debye's approximation is invalid

when ions can approach to each other to considerably small distance. The length,

$$q = z_\alpha z_\beta e_o^2/2 \epsilon kT, \qquad (1\text{-}2)$$

is a critical radius, according to Bjerrum, where z is the valency of ion indicated by the subscript, ϵ the dielectric constant of the medium, e_o the elementary charge taken as the absolute value. If the distance between two ions r' is larger than q, the Debye approximation applies in its original form, but if $r' < q$ a correction has to be introduced. The concept of ion-pairing was devised for tackling such a correction term and Bjerrum treats an ion β which is present in the spherical shell (radius q) as "associated by the central ion α." He analysed activity data and obtained much more reasonable value of ionic radius than by direct application of the Debye-Hückel theory, especially for bi-bivalent electrolytes. A feature of the Bjerrum treatment is that it ascertains the existence of undissociated molecules in strong electrolyte solutions. Experimental evidence accumulated more recently supports Bjerrum's assertion.

The Bjerrum model is essentially an electrostatic one based on Coulombic law, just as Debye-Hückel's model that carried a tendency to discount any specific chemical explanation. It is of course questionable whether short-range interaction can be safely ignored when two ions approach very close to one another.

The phenomena of imcomplete dissociation seem to be of importance in the field of polyelectrolyte solutions. The macro-ions carry generally numerous charges, the potential of which is considerably higher than that of simple ions. Therefore, a higher fraction of the counter-ions will be "associated" by the macro-ion. Wall et al.[17] demonstrated the association in an elegant manner. However, there is a trend to ascribe observed deviation of polyelectrolyte solutions from the ideality to overestimated "counter-ion association" without reference to its mechanism. It is hoped that the convincing theoretical approach will be formulated. A method presented by Bjerrum may also be powerful in this case.

In the above, it has been briefly mentioned how thermodynamic interpretation of electrolytic solutions has been developed. The considerations are limited to the method which employs the Poisson equation as a starting point and to the topics which are of important significance in dilute solutions of polyelectrolytes, a subject of this present record.

In an attempt to obtain a better understanding of polyelectrolyte solutions, our emphasis will be on comparison between simple and polymeric electrolytes: the method applied to the former will be used for the latter, with necessary modifications. This way of approach to the problem, we believe,

is an essentially indispensable one to our purpose. In the following chapters, based on a point of view proposed by Wicke and Eigen we present discussions on a treatment which takes the interionic interaction into account and on its comparison with experimental data. In Chapter 2, the treatment will be introduced, paying attention to the comparisons with theories of simple electrolyte solutions and with other theories of polyelectrolyte solutions. (The writer wishes to thank Mr. M. Hosono for his kindness to grant permission to quote his calculation on the potential distribution.) In Chapter 3, the treatment will be checked with potentiometric titration data and the extension of a macro-ion in solution will be estimated. Furthermore the dependences of the extension on temperature, polymer- and salt-concentrations will be obtained. In Chapter 4, the viscosity-concentration curves of polyelectrolyte solutions will be analysed from a stand-point presented in Chapter 2. In Chapter 5, the electrophoresis of a synthetic polyelectrolyte will be described with a main purpose to check the validity of Debye-Henry relation, which will be followed by Chapter 6 dealing with two-component system composed of two kinds of polyelectrolytes. The boundary anomalies of electrophoresis will be interpreted in terms of interionic interaction, topics in Chapter 2. Chapter 7 is to give an approach to small ion binding of poly(vinyl alcohol), which was found to migrate in an electric field just as polyelectro-

lytes. The general discussion will be given in Chapter 8, in which some features of polyelectrolyte solutions in general and possibilities of further advancement and of another way of approach in this field will be described.

CHAPTER 2

ELECTROSTATIC INTERACTION IN DILUTE SOLUTIONS OF POLYELECTROLYTES

§ 1. Introduction

The reputation, which the Debye-Hückel (D-H) theory of dilute solutions of simple electrolytes[5] has enjoyed, is attributed to its insight into nature of interionic interaction, as mentioned in Chapter 1. The fundamental assumption is that the ions do not behave as essentially independent entities and a concept of "ionic atmosphere" is deduced: the mean thickness, $1/\kappa$, Debye's characteristic length, is related to the ionic strength introduced by Lewis and Randall,[18] which had been a characteristic measure of electrostatic interaction in dilute solutions of strong electrolytes. The validity of this theory is most reasonably accepted as a limiting law because any convincing theoretical arguments as well as experimental evidences against this validity are completely lacking.

On the other hand, in the field of polyelectrolytes, most of the earlier works of a theoretical nature[19] and interpretation of existing experimental data can not be satisfactory enough to furnish well-established picture of the solutions. The situation, which will be encountered in treating the problem, is obviously complicated, much more than that in the branch of simple electrolytes. This is due to

the numerous charges and the pronounced volume exclusion effect of the macro-ions, which we believe are most important factors to be taken into consideration in establishing a comprehensive theoretical point of view. Paying attention to first of these, we will notice that almost of all the earlier works have neglected, either intentionally or unintentionally, the interaction between macro-ions except that the volume to be apportined to each macro-ion was assumed to be determined by the polymer concentration and the omission of inter-macro-ion interaction might be a source of the failure in giving a successful explanation. This will become clear if we reflect upon that Debye and Hückel take account of interaction between a central ion and all other ions and even then their success is limited to electrolytes of low valency. Formulation of a theory which takes notice of the interionic interaction including inter-macro-ion interaction, therefore, is of great interest and of urgent necessity.

To formulate this kind of interaction, distributions of all species of ions present in the polyelectrolyte solutions have to be decided. The simplest way is to assume that all small ions and macro-ions except a central ion are point-charges and obey the Boltzmann distribution. This is only a direct application of Debye's second approximation and means taking the macro-ions into consideration in summation of the definition of "usual" ionic strength. This simplification,

however, would be definitely so far away from reality because the volume effect, that was mentioned above, is neglected.

A distribution formula, which was presented by Wicke and Eigen (W-E)[8] with the intuitive introduction of the volume exclusion effect of simple ions, invites our attention. Though it involves rather crude approximations, the theory constructed thereon represents an extension of the D-H theory and can explain concentration dependences of activity coefficient, heat of dilution, and specific heat of simple electrolytic solutions over a wide range of concentration with a few parameters. This means that the theory treats the volume exclusion effect of ions and simultaneously, the interaction between them, though in a less accurate way of reasoning. Therefore it can be expected that its application to our problem is a more satisfactory approximation to the truth than the point-charge approximation.

In this chapter, a treatment of dilute polyelectrolyte solutions will be presented in which electrostatic interaction between all species of ions including macro-ion will be dealt with by a modified W-E's ionic distribution formula. An interpretation will be given of anomalies experimentally found to which earlier explorations had failed to give a satisfactory explanation, through the omission of inter-macro-ion interaction or because of the point-charge approximation. Moreover a formulation of the activity coefficient of macro-ion will

be given, to which most of the previous theories did not give access.

§ 2. Preliminary Considerations

Polyelectrolytes have the dual character of electrolytes and macromolecules. It is only a one-sided description to apply the W-E theory in its original form to discuss the inter-ionic interaction, that is, to assume the macro-ion as a rigid sphere. By "a character of macromolecules" it is meant here that the molecular expansion in solution (at extreme dilution) depends on the repulsive interaction between the ionized groups attached on the polymer chain. This has been well-established by more recent work and has been a focus of the previously published treatments.[19] This intra-macro-ion interaction, in our treatment, is formulated by use of a model analogous to that developed by Hermans and Overbeek (H-O).[19] They originally assumed a uniform charge distribution inside the macro-ion. Their treatment is, according to Schneider and Doty,[20] a reasonable approximation except at a low ionic strengths. This experimental result is quite understandable since at higher ionic strengths due to the shrinking of the polymer coil with increasing concentration of added salt, the charge density in the coil increases, provided that the total number of charges in the coil remains constant, and therefore the uniform distribution will be approached. As the viscosity of polyelectro-

lyte solutions shows, on the other hand, the macro-ions have an effect on the molecular extension essentially equivalent to that of the small ions of added simple salt. Therefore we are led to a conclusion that assuming a uniform distribution is not so serious at non-extreme dilution as it is generally supposed to be at extreme dilution. (In this respect, we must mention the Harris-Rice (H-R) theory,[21] that aimed at removing this assumption by adopting a discrete charge distribution. Their point-charge approximation, we consider, would be much more inadequate than the uniform distribution of charges inside the macro-ion.)

Next we turn to the interionic interaction. The distributions of all species of ions are assumed to obey one of W-E's formula, all small ions being taken as rigid spheres and macro-ions as spherical. According to W-E, the work W_{ij} required to bring an ion j from infinity to a distance r (potential ψ) from a central ion i is given by

$$W_{ij} = (e_j - \rho_j v_j)\psi_i \ , \qquad (2\text{-}1)$$

when the volume exclusion effect is considered only between the ions with charges of the same sign, and e, v and ρ denote the charge, exclusion volume, and charge density respectively, and the subscripts i and j represent species of ions. When $v_j \cong 0$, (2-1) becomes

$$W_{ij} = e_j \psi_i \ , \qquad (2\text{-}2)$$

which was a fundamental assumption of the D-H theory. From (2-1), W-E obtained a distribution formula,

$$n_{rj} = n_j \exp(-e_j \psi_i/kT)/\left[1 + (n_j/N_j)\left\{\exp(-e_i \psi_j/kT) - 1\right\}\right], \tag{2-3}$$

where $N_j = 1/v_j$, i.e., the number of sites which the ion can occupy in unit volume of the solution, and n_j is the average number concentration, n_{rj} the number concentration at a distance r from a central ion. (2-3) becomes the Boltzmann distribution, when $v_j \cong 0$ or the concentration n_j is sufficiently small.

Besides (2-3) reviewed above, W-E have treated another distribution formula taking account of the volume exclusion effect between all ions irrespective of the sign of charge. Between these idealized cases would reality lie. Which of these two is to be preferred depends on consideration on the following problems: firstly a phenomenon of simple ion fixation inside the polymer coil and secondly a self-consistency problem. As for the ion fixation, a startling conclusion has been reported that about two-thirds of the counter-ions lose their freedom to get off the polymer coil. Though it remains uncertain whether fixed counter-ions are able to neutralize the charges of ionized groups completely, it is necessary to admit that the polymer spheres and a fraction of the counter-ions can occupy the same space simultaneously. Accordingly we must reject the second formula of Wicke and Eigen and adopt

(2-3) here. As for the second problem it must be mentioned that (2-3) leads to a self-consistent solution. In this equation, $v_j = 0 = v_i$ is assumed for $i \neq j$ and $v_i = v_j$ holds for $i = j$. Therefore the definition of W_{ij} and the symmetry of the system give us $e_j \psi_i = e_j \psi_j$. Thus the superposition of potential is ascertained, which requires the linearization approximation of Poisson's equation. In the original development of W-E theory, this approximation has been adopted as in the case of the D-H theory. On the other hand, when all ions are assumed to exclude to each other, it can be easily shown that $e_i \psi_j = e_j \psi_i$ does not generally hold.

As will be shown later (in § 3), we will linearize the Poisson equation to obtain the potential distribution. This would lay down restrictions on the applicability of our treatment. We fear that only the polyelectrolytes of low charge density can be adequately described. However, this restriction enables us to make a simplifying assumption that there is no difference in the dielectric constant inside and outside the macro-ion.

The macroscopic properties of polyelectrolyte solutions depend on many kinds of contributions to the total free energy. In our treatment, however, the free energy of electrostatic nature will be assumed to be the predominant factor from which thermodynamic functions will be calculated. This assumption is open to criticism but clearly serves to attain a fuller

knowledge of the radical difference between simple and polymeric electrolytes.

§ 3. Electrostatic Potential

To calculate the electrostatic potential using the Poisson equation

$$\Delta\psi = -4\pi\rho/\epsilon \quad , \qquad (2\text{-}4)$$

where ψ and ρ are the potential and charge density at a distance r from a central ion and ϵ denotes the dielectric constant of the solvent, the following assumptions are made.

(A) The macro-ion is taken as a sphere of radius R, in which exist Z negative ionized groups (monovalent), and λ counter-ions (monovalent). The macro-ion acts on the other ions $Z - \lambda = \alpha$-valent negative ion.

(B) The α effective negative charges inside the macro-ion are uniformly distributed and hence, its charge density is given by $-\alpha e_o/\bar{v}_p$, where $\bar{v}_p$ is the exclusion volume of the macro-ion.

(C) The distributions of all ions, i.e., macro-ions, counter-ions, ions of foreign salt (1-1 type), are approximated by a modified W-E's formula (2-3), which assumes exclusion volume effects only between ions of the same sign and origin. (Later we use Boltzmann's formula as a special case of that of W-E for simple ions, but the general description is given here.) ρ is assumed to be given by the sum of the

ionic charge density of each sign and origin.

If we denote the average number concentration of ions by n, the number concentration at a distance r from a central ion by n_r, the volume of ion by v, the origin of ion by two subscripts p (polymer) and s (salt) and the sign of charge by subscripts + and −, we obtain the expressions for the distributions of four species of ions from (2-3), when the presence of foreign salt gives rise to no change in the number of the fixed small ion,

$$ {}_{p}n_{r}^{-} = \frac{n_p \exp(\alpha x)}{1 + (n_p/N_p^{-})(\exp(\alpha x) - 1)} , \qquad (2\text{-}5) $$

$$ {}_{p}n_{r}^{+} = \frac{n_p \alpha \exp(- x)}{1 + (n_p \alpha/N_p^{+})(\exp(-x) - 1)} , \qquad (2\text{-}6) $$

$$ {}_{s}n_{r}^{-} = \frac{n_s \exp(x)}{1 + (n_s/N_s)(\exp(x) - 1)} , \qquad (2\text{-}7) $$

$$ {}_{s}n_{r}^{+} = \frac{n_s \exp(-x)}{1 + (n_s/N_s)(\exp(-x) - 1)} , \qquad (2\text{-}8) $$

where $x = e_o \psi / kT$.

For $r > R$, ρ is given by

$$ \rho = e_o({}_{p}n_{r}^{+} - \alpha\, {}_{p}n_{r}^{-} + {}_{s}n_{r}^{+} - {}_{s}n_{r}^{-}). \qquad (2\text{-}9) $$

The higher terms than the second in the expansion of (2-5), (2-6), (2-7) and (2-8) as a power series of x being neglected,

a spherical symmetry of ionic distribution and boundary conditions ($\psi = 0$ at $r = \infty$ and the continuities of the potential and the electric induction at the surface of the central ion) give from the linearized Poisson equation,

$$\psi_1 = - \frac{\alpha e_o}{\epsilon} \frac{1}{1 + \kappa R} \frac{1}{r} \exp(-\kappa(r - R)), \quad (2\text{-}10)$$

with

$$\kappa^2 = \frac{4\pi e_o^2}{\epsilon kT} \left\{ \alpha n_p (\alpha m_p^- + m_p^+) + 2 n_s m_s \right\}, \quad (2\text{-}11)$$

where

$$m_p^- = 1 - n_p/N_p^-, \; m_p^+ = 1 - \alpha n_p/N_p^+ , \; m_s = 1 - n_s/N_s. \quad (2\text{-}12)$$

For $r < R$, where ρ is given by $-\alpha e_o/4v_p^-$, we obtain without using the linearization approximation,

$$\psi_2 = \frac{-\alpha e_o}{2\epsilon R^3} \left(\frac{3 + \kappa R}{1 + \kappa R} R^2 - r^2 \right). \quad (2\text{-}13)$$

The potential around the small ion outside the macro-ion ψ_o is given by

$$\psi_o = \frac{e_o}{\epsilon} \frac{1}{1 + \kappa R} \frac{1}{r} \exp(-\kappa(r - \delta)), \quad (2\text{-}14)$$

where δ is the radius of the small ion, and κ is defined by (2-11). (It is a permissible approximation in non-extreme dilution to use a common screening parameter for both macro-ion and simple ion.)

(2-10) and (2-14) are of the same form as the expression

for the potential in the D-H second approximation, but the screening parameter $\varkappa$ defined by (2-11) differs from D-H's by the presence of a correction term corresponding to the volume exclusion effect, (2-22). The same difference is found with a screening parameter in H-R's theory which was defined by eq. 6a in Ref. 21, because it has not made allowance for volume exclusion between ions of the same charge.

(2-13) giving the potential inside the macro-ion simplifies to the expression obtained by Hermans and Overbeek, when $\varkappa = 0$, i.e. for extremely dilute solution. It must be noted that formation of ionic atmosphere inside the macro-ion is not considered in our treatment.

It will be useful to mention here the differences between the H-R theory[21] and ours. In the former, a model which preserves the inhomogeneous (discrete) charge distribution of the macro-ion was used, as already stated, and small ions present around ionized groups were treated to form an ionic atmosphere. The authors pointed out that the dielectric constant inside the macro-ion differs from that outside. Attention has to be also paid to the volume exclusion effect between small ions within a macro-ion and the polymer segment. Firstly, error due to our replacement of the discrete charges by a continuous distribution would become greater with decreasing polymer concentration or with decreasing charge number within the macro-ion. Because we restrict our consideration to polyelectrolytes

of a relatively small number of ionized groups, this error might be fairly large especially at extreme dilution, to which any contradiction with the assumption of the result obtained by applying our treatment to experiments may be ascribed. (See Chapter 3). In this respect, it must be further noted that, in our treatment, the continuous distribution will not be used throughout. The electrostatic free energy will be calculated by using a rigid metallic sphere model for each charge and ionized group within the macro-ion. Because a uniform distribution was assumed for computing the potential, the treatment is evidently contradictory. The extent of the inaccuracy due to this would remain negligible for materials of low charge density. Secondly it must be pointed out that discrimination of two regions, which led Harris and Rice to introduction of an additional term $\chi(r)$ into (2-2), can be safely discarded for such polyelectrolytes as we are interested in. Thirdly the volume exclusion effect that was considered by them can be negligible for the cases considered here, because fraction of counter-ions trapped into the macro-ion sphere will decrease with decreasing density of ionized groups.

§ 4. Electrostatic Free Energy

Before the electrostatic free energy is to be computed, the standard state has to be chosen. The state chosen in or-

dinary electrolyte theory is an ideal one, in which no electrostatic interactions take place. This state will be approached with dilution. On the other hand, as Katchalsky and Lifson have pointed out,[19] polyelectrolyte solutions can never be "ideal", because ionized groups are bound onto the polymer chain and, therefore, they can not diffuse away in the bulk of the solution so that the intra-macro-ion interaction would remain even at extreme dilution. This situation gives rise to a difficulty in the choice of the standard state.

Our standard state adopted here is an entirely hypothetical state, in which each ionized group can behave "ideally". This state will be realized by the hypothetical procedure that polymer chains in the solution are severed in such a way that each fragment contains an ionized group and then the solution is diluted infinitely. This choice is required to describe the "character of macromolecules" and, in addition, enables us to get an insight into the correlation between polymeric and simple electrolytes. The free energy value at extreme dilution remains finite with reference to our standard state and the difference is essentially equivalent to the "polyionic work" referred to by Hayman.[22] Our result mentioned below, that the activity coefficient of macro-ion is not equal to unity at extreme dilution, originates from this "work".

Let us compute the electrostatic interaction free energy by Debye's charging process. The interionic interaction free

energy, $F_{e\ ext}$, is calculated using the difference between the potential, (2-10) or (2-14), and the self-potential of the ion considered. On the other hand, another contribution $F_{e\ int}$ from the intra-macro-ion interaction is calculated using a rigid metallic sphere model for each ionized group and fixed counter-ion which are constrained in the field of potential ψ_2. Then

$$F_{e\ int} = L_p \sum_i \int_0^R \int_0^1 \frac{4\pi r^2 \nu_i \psi_2'(\xi)}{v_p} e_i \, d\xi \, dr, \qquad (2\text{-}15)$$

where ν_i denotes the number of ions of species i in a macro-ion, e_i its charge, ψ_2' the potential at the position of e_i (excluding the self-potential), L_p the total number of macro-ions in the system and ξ the fraction of their final charges which they have at any stage of the integration, and the summation is taken over ionized groups and counter-ions.

Finally, we obtain for the total volume of the solution,

$$F_e = F_{e\ int} + F_{e\ ext} = -\frac{\kappa e_o^2}{3\epsilon}\left\{ L_p \alpha (\alpha \tau(\kappa R) + \tau(\kappa\delta_1)) + 2L_s \tau(\kappa\delta_2)\right\} + \frac{L_p e_o^2}{\epsilon}\left\{ \frac{3\alpha^2}{5R} - \frac{1}{2\delta_1}(Z+\lambda)\right\}, \qquad (2\text{-}16)$$

where

$$\tau(y) = (3/y^3)\left\{\log(1+y) - y + (y^2/2)\right\}, \quad L_s = V n_s,$$

and δ_1 is the mean radius of an ionized group (assumed to

be a sphere) and a counter-ion, δ_2 the mean radius of positive and negative ions of foreign salt and V the total volume of the solution.

When the concentrations of salts and polyelectrolytes approach zero, the terms containing $\varkappa$ become negligibly small and (2-16) simplifies to a modified expression of H-O's theory. When the macro-ion is replaced by a metallic sphere the second brace disappears, and the expression is in formal coincidence with D-H's or W-E's theory.

§ 5. Osmotic Coefficient and Activity Coefficients

When P_i stands for a value the osmotic pressure of (α-valent) polyelectrolyte solutions would have if the solution behaved in an ideal way, the deviation from ideality is measured by the osmotic coefficient g.

Considering that the radius R of a spherical macro-ion is determined by the minimum condition of the electrostatic free energy, $\partial F_e / \partial R = 0$, we obtain by the usual procedure

$$1 - g = \frac{\varkappa e_o^2}{6 \epsilon kT} \frac{1}{n_p(1+\alpha) + 2n_s} \Big\{ n_p \alpha (\alpha \sigma(\varkappa R) + \sigma(\varkappa \delta_1)) + 2n_s \sigma(\varkappa \delta_2) \Big\} \times \left\{ 1 - \frac{(n_p\alpha)^2 v_p^- + (n_p\alpha)^2 v_p^+ + 2n_s^2 v_s}{n_p \alpha^2 m_p^- + n_p \alpha m_p^+ + 2n_s m_s} \right\} , \tag{2-17}$$

where

$$\sigma(y) = (3/y^3)\Big\{ 1 + y - 1/(1+y) - 2\log(1+y) \Big\} .$$

When $n_s \cong 0$ and $\delta_1 \cong 0$ (i.e., $\sigma(\varkappa\delta_1) \cong 1$ and $m_p^+ \cong 1$), (2-17) becomes

$$1 - g = \frac{\alpha \varkappa e_o^2}{6 \epsilon kT (1+\alpha)} \left\{ \alpha \sigma(\varkappa R) + 1 \right\} \left\{ 1 - \frac{n_p \alpha v_p^-}{1 + \alpha m_p^-} \right\}. \qquad (2\text{-}17')$$

With appropriate values, the g-concentration curve is constructed by (2-17') and is shown in Fig. 1. The dashed curve represents the case in which $v_p^- = 0$ is assumed. At higher concentration, the volume effect is increasingly remarkable.

Similarly, the usual thermodynamic routine gives the activity coefficient of counter-ion, γ_g, and of macro-ion, γ_p. They are expressed, when $\partial F_e/\partial R = 0$ is again applied, in (2-18) and (2-19) respectively. For the salt-free solution and

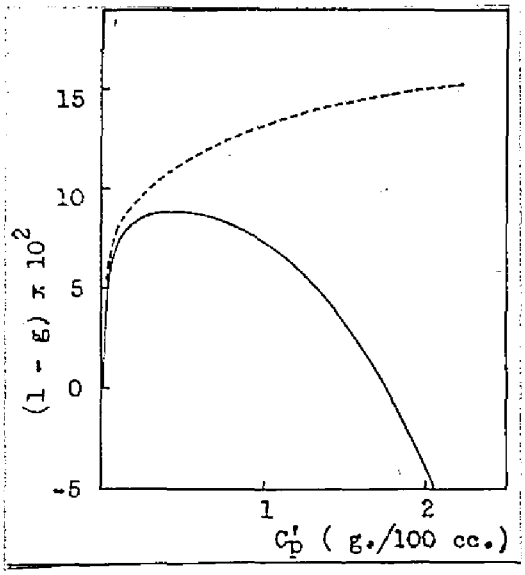


Fig. 1. Concentration dependence of osmotic coefficient g calculated with R = 50A., α =8, the base mol. = 50, the degree of polymerization = 200, T = 288°K and ϵ = 80. The full line is calcd., introducing the volume exclusion of the macro-ion. The dashed line shows the case in which the volume exclusion is not considered.

when $\delta_1 \cong 0$, (2-18) and (2-19) simplify to (2-18') and (2-19').

$$kT\log \gamma_g = -\frac{\kappa e_o^2}{3\epsilon}\left\{ \tau(\kappa\delta_1) + \frac{1}{2}\left[n_p\alpha(\alpha\sigma(\kappa R) + \sigma(\kappa\delta_1)) + 2n_s\sigma(\kappa\delta_2)\right] \times \left(\frac{1 - 2n_p\alpha v_p^+}{n_p\alpha^2 m_p^- + n_p\alpha m_p^+ + 2n_s m_s}\right), \right. \quad (2\text{-}18)$$

$$kT\log \gamma_p = -\frac{\kappa e_o^2}{3\epsilon}\left\{ \alpha^2\tau(\kappa R) + \frac{1}{2}\left[n_p\alpha(\alpha\sigma(\kappa R) + \sigma(\kappa\delta_1)) + 2n_s\sigma(\kappa\delta_2)\right] \times \left(\frac{\alpha^2 - 2n_p\alpha^2 v_p^-}{n_p\alpha^2 m_p^- + n_p\alpha m_p^+ + 2n_s m_s}\right)\right\} +$$

$$\frac{e_o^2}{\epsilon}\left\{\frac{3\alpha^2}{5R} - \frac{Z+\lambda}{2\delta_1}\right\}, \quad (2\text{-}19)$$

$$kT\log \gamma_g = -\frac{\kappa e_o^2}{3\epsilon}\left\{1 + \frac{1 + \alpha\sigma(\kappa R)}{2(1 + \alpha m_p^-)}\right\}, \quad (2\text{-}18')$$

$$kT\log \gamma_p = -\frac{\alpha^2\kappa e_o^2}{3\epsilon}\left\{\tau(\kappa R) + \frac{1}{2}(1 + \alpha\sigma(\kappa R)) \times \left(\frac{1 - 2n_p v_p^-}{1 + \alpha m_p^-}\right) + \frac{e_o^2}{\epsilon}\left\{\frac{3\alpha^2}{5R} - \frac{Z+\lambda}{2\delta_1}\right\}\right. . \quad (2\text{-}19')$$

Fig. 2 is a graphical representation of (2-18') and (2-19'). As in the case of osmotic coefficient, a mimimum appears, which the point-charge approximation as well as the treatments neglecting the inter-macro-ion interaction can not elucidate. That γ_p is not equal to unity at $C_p' = 0$, reflects the char-

acter of charges attached to macro-ions. This deviation from ideality comes from the striking interaction between ionized groups. Recently Kagawa and Nagasawa[23] concluded that "the polyelectrolyte solutions can be considered an ideal solution so far as the macro-ion is concerned." However their metallic sphere model of the macro-ion is intrinsically inadequate to describe the "character of macromolecules." It must be further pointed out that they neglected the free energy contribution from the inter-macro-ion interaction (for example, see their derivation of eq. 14 in Ref. 23) and noted that calculated values of γ_p and γ_g in our notation decrease steadily with the polymer concentration.

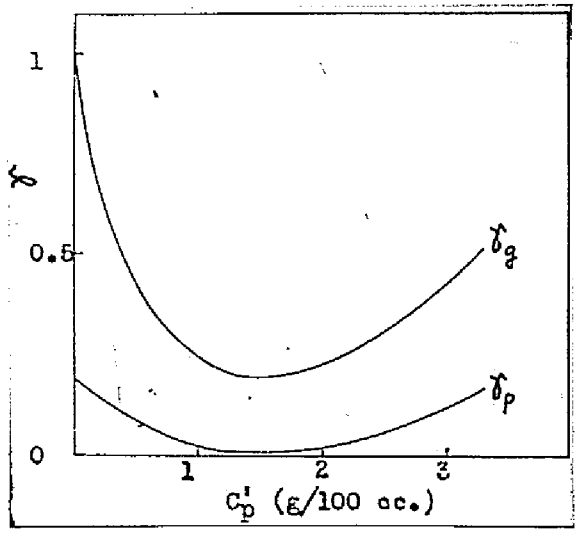


Fig. 2. Activity coefficients of macro-ion γ_p and of counter-ion γ_g with R = 50A., δ_1 = 5A., the base mol.= 50, the degree of polymerization = 200, T = 288°K and ϵ = 80. α = 8 and Z = 9 are chosen for γ_p, and α = 100 for γ_g.

Before comparing these calculated values with experimental results, it must be borne in mind that our calculations have dealt with the electrostatic interaction only, and they do not

provide quantitative information on λ , and the (calculated) individual ionic activity coefficient is only convenient mathematical fiction, which has no physical significance.[24] The electrostatic interaction effect being discussed here and the counter-ion fixation effect seem mainly responsible for very low observed values of these coefficients. If λ hardly depends on the polymer concentration as Wall and his schools have shown,[17,25] however, the concentration dependences of these coefficients could be interpreted at least qualitatively from the predicted courses in Figs. 1 and 2. It is further to be noted that, in salt-free solutions, the volume effect of macro-ions, that is, the molecular extension, depends on the concentration in dilute solutions as the characteristic viscosity-concentration curve shows. The macro-ion is expected to shrink with increasing concentration, so that the values of g and γ_g would be smaller and the minimum points would shift towards higher concentrations, than those calculated with a fixed radius. As for the individual ionic activity coefficient, it is to be noted that a dilemma, which is a natural consequence of trying to measure a quantity which physically does not exist, is in every case confronted and, in the field of polyelectrolyte solutions, is considered to be overcome by postulating that use of the salt bridge allows to determine the ionic coefficient of small ions by electrochemical measurements. To be correct, the mean activity coefficient has to be measured and compared

with the expression which will be derived from (2-18)and (2-19). However, we will continue our discussion on the individual ionic activity coefficient, taking for granted that the postulate mentioned above is practically reasonable, because the mean values have not been reported.

Kern[26] observed that g and γ_g increased with concentration for sodium poly(acrylate) (degree of polymerization, P, = 340) solutions. On the other hand, Kagawa reported the opposite tendencies of these coefficients for sodium carboxymethylcellulose (P = ca. 200) solutions.[27,28] Considering the closeness between degrees of polymerization and between charge densities, the confusing results are not unreasonable. Kern carries out the measurements in high concentration ranges where R hardly varies with concentration and therefore observed the right-hand side around the extreme values in Figs. 1 and 2, whereas Kagawa measured these quantities in a more dilute region.

If the volume effect is considerable, for example, because of a high degree of polymerization, only the tendency of increasing will be observed. Recently, Inoue[29] asserted that g decreased with increasing concentration for linear polyelectrolytes while it increased for branched materials. We noticed that the degree of polymerization of his branched material is much higher than that of the other, which would be expected to give the observed variation of g because of the more

pronounced volume effect.

Moreover mention should be made of the observation that g and γ_g occasionally appear not to converge to unity at $C_p' = 0$.[29,30] This is a radically different feature from that of γ_p referred to above. We should like to point out again that calculated values give the osmotic and activity coefficients in a system containing α-valent, not Z-valent, macro-ions.

Regretfully no determination has not been reported of γ_p[31] until recently, but the differential quantity has been measured indirectly. It is the rate of change of the activity coefficient of the polyelectrolyte component with its concentration, β_{22}^*, which appears in the second virial coefficient. Edsall et al.[32] have shown that the turbidity τ of polyelectrolyte solutions is related to the polyelectrolyte concentration C_p' (g./100 cc.) by the expression,

$$\frac{H\,C_p'}{\tau} = 1/M + (C_p'/M^2)(\alpha^2/2m_3 + \beta_{22}^*), \qquad (2\text{-}20)$$

where $\beta_{22}^* = \partial \log \gamma_2 / \partial m_2$, γ_2 being the activity coefficient of polyelectrolyte component (see Ref. 32 about the definition of the component), m_2 the polyelectrolyte concentration (mol./l.), α the absolute number of the effective charges of a macro-ion, m_3 the concentration of foreign salt (mol./l.), H the Debye factor and M the molecular weight of the polyelectrolyte. They determined the value of β_{22}^* for bovine serum albumin-NaCl aqueous solutions. If we follow their "starred system

of definition of component", in other words, if we take a system composed of one mole of macro-ions (negative), $\alpha/2$ moles of Na^+-ions and $-\alpha/2$ moles of Cl^- ions as a component, we obtain

$$\log \gamma_2 = \log \gamma_p + (\alpha/2) \log \gamma_{Na^+} - (\alpha/2) \log \gamma_{Cl^-} , \tag{2-21}$$

where γ_{Na^+}, and γ_{Cl^-} are the ionic activity coefficients of Na^+- and Cl^--ions respectively. If $\gamma_{Na^+} = \gamma_{Cl^-}$ is assumed,

$$\log \gamma_2 = \log \gamma_p . \tag{2-22}$$

(Note that this relation holds irrespective of the sign of the protein charge.) Therefore

$$\beta_{22}^{*} = \partial \log \gamma_p / \partial m_2 . \tag{2-23}$$

When $\partial R/\partial n_p = 0$, as would be the case for rigid molecules such as bovine serum albumin which do not seem to suffer appreciable change in extension with their own concentration, and because m_s is very close to unity under Edsall's experimental conditions, from (2-19) we obtain for the corresponding quantity at the limit of $C_p' = 0$,

$$(\partial \log \gamma_p / \partial n_p)_{n_p \to 0} = - \frac{\chi' e_0^2 \alpha^2}{12 \epsilon n_s kT} \left\{ (2\sigma(\chi'R) - 1/2)\alpha^2 + \right.$$

$$\left. \alpha\sigma(\chi'R) + \alpha/2 - 4n_s v_p^{-} \right\} , \tag{2-24}$$

with the Debye reciprocal length, χ'.

Because α is taken as the absolute value, $(\partial \log \gamma_p / \partial n_p)_{n_p \to 0}$

does not depend on the sign of the protein charge. This is in harmony with Edsall's observation that $\beta_{22}^{*} - \alpha$ curves are symmetrical about $\alpha = 0$. For quantitative comparison of our present treatment with experiment, we compute R using (2-24) and the observed values of β_{22}^{*} after changing the unit of concentration. The results are tabulated in Table 1. For comparison, the closest distance of approach, "a", is also shown, which is evaluated by a corresponding relation obtained from the D-H second approximation, i.e., the point-charge approximation for all ions except a central ion,

$$\left(\partial \log \gamma_p / \partial n_p\right)_{n_p \to 0} = - \frac{\alpha^3 e_o^2 (1+\alpha)}{8 \in n_s kT} \frac{\kappa'}{1+\kappa' a} . \qquad (2\text{-}25)$$

Table 1. Radius of Bovine Serum Albumin from β_{22}^{*}

ionic strength (salt: NaCl)	α (<0)	β_{22}^{*}	R (A.)	a (A.)
0.183	10	+250	10	imaginary
	20	-300	10	120
0.033	10	-400	25	30
	20	-4000	25	120
0.003	10	-12500	40	50
	20	-55500	70	160

"a" would correspond to the radius of the protein when $m_2 \to 0$. The radius of this albumin is reported to be of the

order of 30 - 100 A., assuming it to be a sphere.[33,34] Table 1 shows that our treatment represents an improvement upon the D-H theory, which renders us an imaginary value for the radius in the case of positive β^*_{22}. The positive value, though found frequently by Edsall et al., can not be elucidated unless we admit that macro-ions can contribute to formation of the ionic atmosphere just as small ions do, and furthermore, the point-charge approximation is discarded. γ_p formulated by Kagawa-Nagasawa[23] also can not provide the positive value of β^*_{22}.

Marked difference has been found between the second virial coefficient B and the so-called Donnan term, $\alpha^2/2m_3$, which has been interpreted in several ways. Schneider and Doty[20] calculated the second virial coefficient using the Flory theory[35] and obtained the good agreement with the experimental value. They regarded this agreement, that was also confirmed by Strauss and Wineman[36] recently for long-chain polyphosphates in sodium bromide solutions, as an evidence that "the interaction of the polymeric ion is essentially the same as that of neutral polymer molecule." This seems to be in accordance with H-R's observation. Such a way of reasoning, it must be noted, is equivalent to the rejection of (2-20), which is a general expression of the electrostatic interactions, and is closely connected to lack of the experimental study and theoretical interpretation concerning the activity coeffi-

cient of macro-ion. On the other hand, Edsall et al.[32] and Trap and Hermans[37] attributed the difference between $_{\Lambda}B$ and the Donnan term to the activity correction term containing β^{*}_{22}. (Strauss and Wineman[36] seem to follow this way of approach in asserting that β^{*}_{22} should have a large component which is inversely proportional to the concentration of the foreign salt.) It is clear that our interpretation is in line with these. (Inagaki et al.[38] introduced a concept of association of simple ions with the macro-ions to reach agreement. Lumping the disagreement into an "effective" charge of macro-ion, however, is definitely doubtful.)

The osmotic and activity coefficients are found to have the tendency that they decreased at first and then through a minimum, subsequently increasing with the polymer concentration. This tendency has been also of occasional occurence in the field of simple electrolytes, and is not peculiar to our case. The existing theories of Osawa-Imai-Kagawa[19] and of Kagawa-Nagasawa[23] failed to give an explanation on the above mentioned increase. The situation was similar to that which existed with respect to simple electrolytes before the advent of the Wicke-Eigen theory, when it seemed hopeless to explain the thermodynamic behaviours in wide ranges of concentration. The results obtained by application of W-E distribution formula implies retrogression of ionic atmosphere, which is caused by the volume exclusion of ions and occurs in the smaller con-

centration range, the greater the volume exclusion effect becomes. This effect is markedly important in the field of polyelectrolytes. Spherical particles of radius 5A. come in contact with each other at about 3 mol./l., and those of 50A., which is usually the case in polymer solutions, at about 3×10^{-3} mol./l. This illustration shows that the volume effect of polymers ceases to be negligibly small at much lower concentration than expected in the simple electrolytes. (It also elucidates a disadvantage of the point-charge approximation mentioned above.)

We wish to conclude this section by expressing our belief that there is no essential distinction between polymeric and simple electrolytes except a fundamental characteristic, i.e., attachment of charges to the polymer chain, in so far as the osmotic and activity coefficients are concerned.

§ 6. Heat of Dilution

In the preceding section, the interionic interaction in dilute solutions of polyelectrolytes was shown to be much more striking than that in simple electrolyte solutions. Deviation from ideality was discussed in terms of the osmotic coefficient and activity coefficients. Heat of dilution will also serve to manifest the importance of the interaction.

(2-16) giving the electrostatic free energy enables us to formulate the expression for the heat of dilution of polyelectro-

lyte dilute solutions ΔH_p. Using $\partial F_e/\partial R = 0$ and assuming the independence of δ_1 from temperature, then we obtain for the salt-free solution

$$\Delta H_p = \frac{L_p \varkappa e_o^2}{3\epsilon}\left\{\alpha\epsilon'\left[\tau(\varkappa R) + (1/2)\sigma(\varkappa R)\right] + (3/2)\alpha V' + (3/2)(\epsilon' + V')\right\} - \frac{L_p e_o^2 \epsilon'}{\epsilon}\left\{\frac{3\alpha^2}{5R} - \frac{Z+\lambda}{2\delta_1}\right\}, \qquad (2\text{-}26)$$

where

$$\epsilon' = 1 + \frac{T}{\epsilon}\frac{\partial\epsilon}{\partial T} \quad \text{and} \quad V' = \frac{1}{3}\frac{T}{V}\frac{\partial V}{\partial T}.$$

The D-H theory gives the heat of dilution of dilute simple electrolyte solutions ΔH_o, which is given by

$$\Delta H_o = \sum_i L_i \varkappa' e_i^2(\epsilon' + V')/2\epsilon, \qquad (2\text{-}27)$$

where L_i is the total number of ions of species i in the system. For water at 25°C, $\epsilon' = -0.370$ according to Wyman[39] and V' is reported to be -0.025 by Dorsey.[40] Using these values, ΔH_o should be always negative. (In more concentrated solutions a positive heat of dilution has been observed and successfully interpreted by the W-E theory.[41])

On the contrary, (2-26) indicates that ΔH_p at sufficiently great dilutions is positive when $Z \gg \lambda$ and $R < 6\,\delta_1 Z/5$,

because the first brace regarding the interionic interaction is negligible compared to the other expressing a contribution from the intra-macro-ion interaction. (The condition on R can in the usual cases be fulfilled.) This term becomes predominant at high concentrations, where R would not vary with the concentration so markedly as in the more dilute solutions, and then ΔH_p becomes positive. The prediction is partly supported by Schulze,[42] who for the first time carried out the determination of intermediate heat of dilution in a very low concentration range and obtained the positive values.

According to Schulze, the intermediate heat of dilution of poly(vinyl-N-butylpyridinium bromide) increased very steeply with the concentration, so that the extrapolation to the extreme dilution was impossible. This is quite understandable since his material was completely neutralized and therefore α was supposed to be very large, which appeared in a term giving the concentration dependence (the first brace in (2-26)). Another of his observations that the absolute value of the heat of dilution of polysalts was much greater than that of the corresponding simple electrolyte, N-butylpyridiniumbromide, is also due to the presence of numerous charges of the polysalt.

Schulze's conclusion, that the positive value should be related to the dissociation of Br^--ions bounded in the polymer sphere, seems really questionable. As mentioned above, Wall

et al. have shown that the fraction of bounded small ions hardly depends on the polymer concentration. Even if Wall's experiment is in fault, the increase of free Br^--ions with dilution is expected to contribute to the total thermal balance in the same way as simple electrolytes with the dilution. In other words, this contribution should be negative. Thus the positive value, it is clear, should be interpreted exclusively in terms of the intra-macro-ion interaction.

§ 7. Discussion

In this chapter, electrostatic potential and thermodynamic properties of polyelectrolyte solutions have been discussed. The expressions contain those obtained for simple electrolyte as a limiting case, when the macro-ion is replaced by a rigid metallic sphere, and reduce to the D-H theory as another limiting one, when the volume effect of ions is neglected. Our emphasis was put on the character of macromolecules, a feature by which simple and polymeric electrolytes can be radically distinguished.

In an attempt to compare our treatment with experiment, there leaves something to be desired. It comes from the two-handed nature of our treatment. The left hand must know what the right hand does: in order to determine the thermodynamic quantities, the concentration-molecular dimension (R) relationship must be well-established, because in all of the expressions

for thermodynamic quantities derived, R remains as an adjustable parameter. Qualitative discussion on this relationship was a subject of earlier works, and a conclusion, that R increases steeply with decreasing polymer concentration, has been drawn from the reduced viscosity curve. However, the interpretation of the relationship seems to us definitely unsatisfactory and the quantitative expression of the variation of R is still lacking. Therefore, we can not help being satisfied with the qualitative comparison of our formula with expeimental results as we presented here.

In the next chapter, we proceed to obtain the information of R, especially of its concentration dependence, from the potentiometric titration curves of the polyelectrolyes. Such an analysis may be applied to the quantities discussed here, at least in principle. However, the difficulties encountered in determining the osmotic coefficient by osmometry, and the complete absence of knowledge on the activity coefficient of macro-ion, and the difficulties in measuring the heat of dilution sufficiently precisely make us feel it inappropriate to follow this way of analysis. It is hoped that alternative experimental methods, by which these deficiencies can be overcome, are developed.

Apart from rather crude approximations involved in the W-E theory itself, there are some points to be discussed in connection with the validity of our application of the W-E

distribution formula to the polyelectrolytes. Additivity of the charge density, (2-9), is justified only for the case when no space-requirement can be assumed between all species of ions. The inaccuracy due to this would increase with increasing space-requirement. Therefore, our treatment would success in describing the behaviours of polyelectrolytes of low degree of polymerization. Moreover, as the molecule expands in more dilute concentration-range, the pronounced space-requirement would invalidate our treatment. Obviously the error reaches its maximum when the extreme dilution is approached. It is to be emphasized that the assumption of the additivity would be a better approximation for our case that the volume exclusion is taken into consideration between ions of the same sign and origin, than for an extreme case where all ions require the exclusion volume.

Moreover, when the space-requirement is striking, the assumption of spherical symmetry of ionic distribution has to be reexamined. Removal of this assumption, however, would make the mathematical treatment of the Poisson equation very complicated. Accordingly the symmetry must be regretfully assumed, the inaccuracy of which increases also with decreasing degree of polymerization.

It must be mentioned, furthermore, that it was upon the work W_{ij} that Wicke and Eigen fixed their attention in an attempt to improve on the D-H theory. One other of such attempts,

as is well known, was to obtain a more accurate solution of the exact Poisson-Boltzmann equation.[13] This has been followed in the efforts to develop a theory of polyelectrolytes, the electrostatic potential of which is usually supposed to be very high because of the numerous charges, and the removal of the assumption $e\psi < kT$ seems to be regarded as an essential step. (See, for example, Alfrey-Berg-Morawetz, Lifson-Katchalsky, Osawa-Imai-Kagawa, Wall-Berkowitz and Lifson in Ref. 19.) In our opinion, however, the success by Wicke and Eigen shows that $e\psi/kT$ is not always a steeply increasing function with ionic concentration for all important values of the distance from a central ion, against the generally accepted expectation. Therefore, we can adopt the approximation unless we expect that the validity of our treatment can be extended to the polyelectrolytes of high charge density, and to the higher concentration.

These considerations indicate that it is difficult to estimate the resultant error of our treatment at present. It is most likely, however, that it would fail for materials of high charge density and in more concentrated solutions. Within these limitations, our formula may be used for smoothing and extrapolating experimental results if the adjustable parameter, R, can be determined independently: it will be possible to determine the characteristic values of the activity coefficient and heat of dilution at extreme dilution.

The materials which will be referred to later are of rela-

tively lower charge density than those attracting public attention generally are. This limitation does not deprive our assertion on the importance of interionic interaction of its generality, but enables us to get a glimpse of the much more predominant effect which is certainly expected to appear in the case of typical polyelectrolytes. Moreover we know many compounds, the shape of which in solutions is quite different from the spherical model adopted here. However, the basic idea presented in our treatment, formation of an ionic atmosphere, seems to remain to be useful in interpreting almost of all macroscopic properties of the solutions, irrespective of the mathematical treatment.

CHAPTER 3

POTENTIOMETRIC TITRATION AND EXTENSION OF MACRO-ION

§ 1. Introduction

A great deal of research has been accumulated on the potentiometric study of polyelectrolytes. Attention has been paid on typical and weak polyelectrolytes, the experimental results of which fit an empirical relation proposed by Katchalsky[43] as follows,

$$pH = pK + n \log \frac{\alpha'}{1 - \alpha'} \quad , \qquad (3\text{-}1)$$

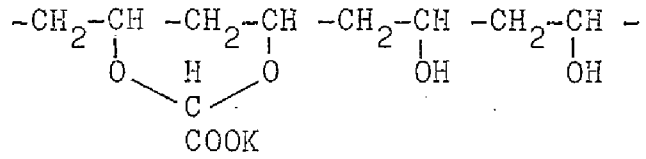
where α' is the degree of neutralization, pK the apparent dissociation constant, n a constant, and pH has the usual meaning. Considering assumptions involved in the derivation of (3-1), it seems interesting to study whether (3-1) also can describe the titration curves of polyelectrolytes of larger dissociation constant. We have carried out the potentiometric study of poly-(vinyl alcohol) partially acetalized with glyoxylic acid, which was previously viscometrically studied by Nakajima et al.[44]

During the neutralization of polymeric acids or bases there is a continuous variation in the strength of the ionizable group. This is clearly due to the electrostatic effects of the increasing number of charges on the macro-ion, and must depend largely on the molecular extension. Therefore, if the electrostatic effect is formulated as a function of the molecular extension, the latter can be estimated using the titration

curve. In Chapt. 2, we have discussed the electrostatic interaction in dilute solutions of polyelectrolytes and obtained an expression for the electrostatic free energy, that makes it possible to get an information of the molecular extension in dilute solutions, in other words, to obtain knowledge of the concentration dependence of the extension.

§ 2. Experimental

(A) Materials. Fractionated poly(vinyl alcohol) was acetalized in the sulphuric acid-water mixture with glyoxylic acid, which was obtained by electrolytic reduction of oxalic acid. The details of these reactions are given in Ref. (44). Removing sulphuric acid by dialysis after the reaction, the polymer solution was added potassium hydroxyde and precipitated in methanol. After purifying the polymer by methanol in the Soxhlet extractor, the solid polymer was dried at room temperature and under diminished pressure. The degree of acetalization was determined by conductometry; the carboxyl group content, S, expresses the number of carboxyl groups per 100 basic molecules of poly(vinyl alcohol). The structural formula of this polyacid is as follows:



The degree of polymerization was determined by the viscosity

measurement of poly(vinyl alcohol) in water at 30°C, which was separated after blanck treatment. The relation used for the calculation was $[\eta] = 7.5 \times 10^{-4} P^{0.64}$ where $[\eta]$ was the limiting viscosity number and P the degree of polymerization.

(B) Potentiometric Titration. The experiment was performed at room temperature (about 25°C) using a pH meter, Model P, Horiba Instrument Inc., and a glass electrode. The sensitivity of the potentiometer was 0.01 pH unit and the reproducibility of the data was 0.03 pH unit. The polymer, stocked as the alkali salt, was titrated with hydrochloric acid, the end point being determined by conductometry.

(C) Experimental Results. In Fig. 3, examples of titration curves are given. The curves differ clearly from those of weak polyacids such as poly(methacrylic acid) or poly(acrylic acid) in their shape, which is rather close to that of simple strong acids. (3-1) does not fit our experimental results and a correction term has to be introduced. Katchalsky has assumed

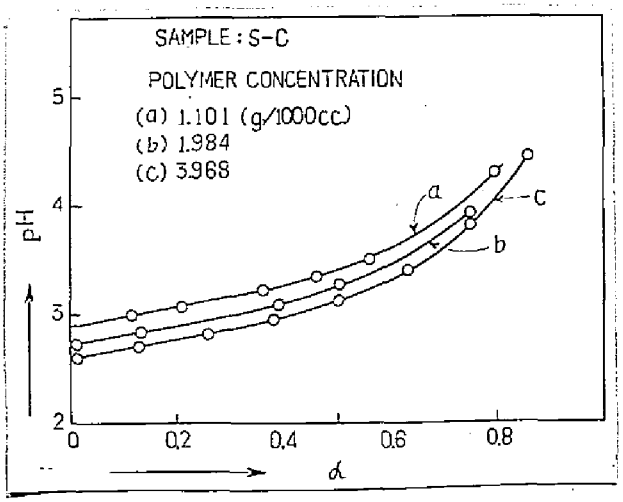


Fig. 3. Titration curves of PVAG (I). (Polymer concentration dependence.).

that in the dissociation equilibrium of weak acid HA, i.e., $HA \rightleftarrows H^+ + A^-$, the concentration of A^-, (A^-), is equal to the concentration of the produced salt, (B^+), and obtained (3-1). This assumption, clearly, fails in the case of fairly strong acid and it is reasonable to introduce a correction term due to self-dissociation of the ionizable groups. Thus $(A^-) \fallingdotseq (B^+) + (H^+)$. Expressing the total concentration of ionizable groups by (C), we obtain

$$pH = pK + n \log \frac{\alpha' + (H^+)/(C)}{1 - \alpha' - (H^+)/(C)}$$

$$\equiv pK + n \log \frac{\alpha''}{1 - \alpha''} \quad . \qquad (3\text{-}2)$$

Because $\alpha' + (H^+)/(C)$ denotes the ratio of the number of ionized groups to the total number of ionizable groups, it can be regarded as an extended degree of neutralization α''. As is shown in Fig. 4, (3-2) is found to fit our data very closely.

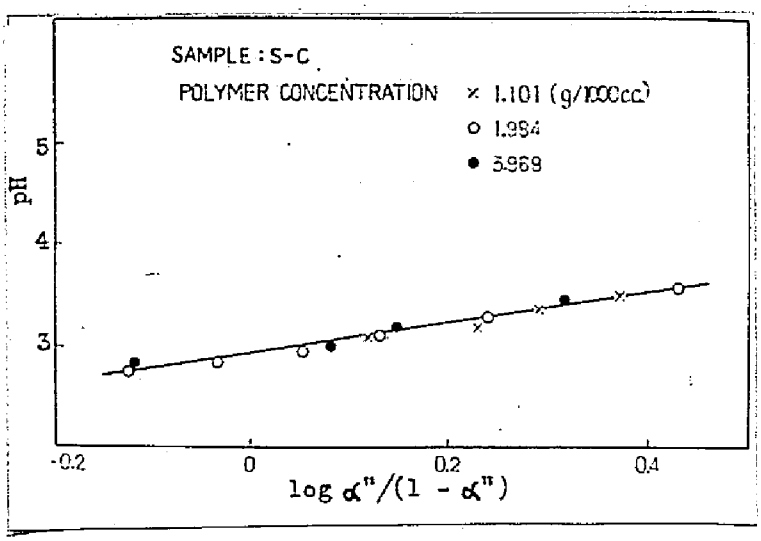


Fig. 4. Titration curves of PVAG (II).

Using (3-2), pK, pH at $\alpha'' = 0.5$, was determined and tabulated in Table 2. From this table, it is found that pK increases with increasing S and hardly depends on the polymer concentration and the degree of polymerization. (Note the marked con-

Table 2. Dissociation Exponent of PVAG

sample	P	S (mol.%)	C_p (g./1000 cc.)	pK
S-A	2150	12.08	4.030	3.33
			2.015	3.33
			0.918	3.33
S-7	1700	5.82	2.916	2.60
			0.972	2.60
S-8	1700	3.46	6.940	2.55
			3.470	2.55
			2.082	2.45
S-C	970	10.80	3.968	2.90
			1.984	2.90
			1.101	2.90
S-1	890	5.73	4.058	2.90
			2.960	2.93
			1.976	2.95
			0.998	2.85
S-2	890	2.55	7.364	2.50
			3.682	2.53
			2.210	2.65

C_p: polymer concentration, S: carboxyl group content.

centration dependence of pK, when determined by (3-1). See Fig. 3.) Katchalsky noticed that pK of poly(methacrylic acid)

determined by (3-1) was concentration-dependent and introduced an activity correction, which according to him can be derived from the simple D-H theory. His treatment, however, seems incomplete because the ionized groups also were considered to form the ionic atmosphere in the same manner as simple ions, in other words, because he did not take the "character of macromolecules" mentioned in Chapt. 2 into consideration.

§ 3. Extension of Macro-Ion

In Chapt. 2, a radical difference between polymeric and simple electrolytes was pointed out that the charges on the polymer chain can not diffuse away into the bulk of the solution. Therefore the local charge density in the polymer sphere would remain at a higher value even in the extreme dilution than that in the dilute solutions of simple electrolytes. Accordingly the ionizable groups are always suffering from strong interaction of electrostatic nature. We believe that the difference in potentiometric behaviours of these two kinds of electrolytes is largely due to this interaction effect, which would be completely absent in the ideal solutions of simple electrolytes, i.e., in the infinite dilution. (This effect, though not so striking in simple electrolyte solutions, becomes large with increasing ionic concentration. For weak electrolytes, the effect would be negligible and the Ostwald dilution law holds,

whereas, for strong ones which produce a great number of ions, this is not the case.) The electrostatic free energy change of polyelectrolyte solutions, ΔF_e, which can be given by (3-3), is an expression for this interaction.

$$pH = pK_o + \log \frac{\alpha''}{1 - \alpha''} + 0.434\, \Delta F_e / kT, \qquad (3\text{-}3)$$

where pK_o is the intrinsic dissociation exponent of a single ionizable group in the uncharged molecule, i.e., the limiting value of pK for zero degree of ionization. From this definition pK_o is expected to be equal to pK of the corresponding monomeric acids or bases in their ideal state. (This definition follows from our choice of the standard state of the free energy. Katchalsky et al.[43] have found that pK_o is incidentally very close to the dissociation exponent of the monomeric acids or bases. This closeness shows the convenience of our choice.) For our material, however, it is difficult to separate the monomeric acid. Therefore, a conventional method is used here: graphical extrapolation of pK to zero carboxyl group content. The variation of pK with S is shown in Fig. 5, which is constructed on the basis of a conclusion mentioned above that pK is concentration-independent. From this figure, we obtain $pK_o = 2.50$, which diverges from the dissociation exponent of glyoxylic acid (3.22). This difference may be due to the presence of electronegative oxygen atoms in the acetal compound.

This evaluation of pK_o involves approximate extrapolation and assumptions, which we can dispense with when the monomeric acid can be easily prepared. However we will regard the value obtained here as correct and will proceed to the following considerations on the extension of a macro-ion, which can be estimated from the titration curve and pK_o.

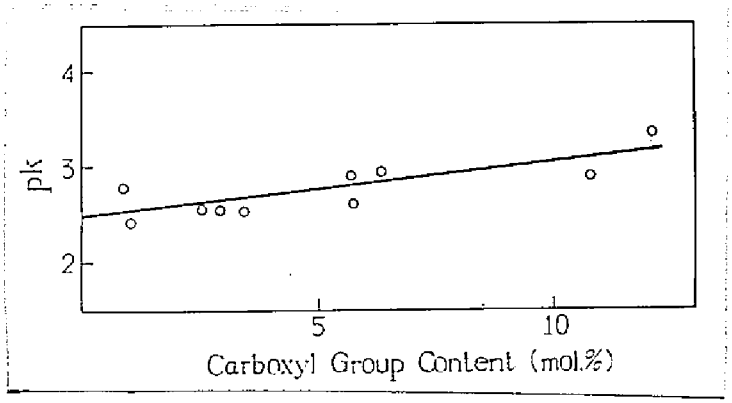


Fig. 5. Variation of pK with carboxyl group content.

ΔF_e in (3-3) can be formulated by partial differentiation of F_e, (2-16), with respect to Z using a condition, $\partial F_e/\partial R = 0$. For the sake of simplicity, the following assumptions are made, based on the experimental results by Wall and his associates:

(A) The fraction of fixed counter-ions, regarded as the degree of ion-pair formation in our treatment, is equal to α'' when $\alpha'' < 0.4$. The number of fixed ions in a macro-ion, λ, is given by Z^2/P.[17]

(B) λ does not depend on the polymer concentration.[17]

Then for the salt-containing solutions, we obtain

$$\Delta F_e = -\frac{e_o^2}{\epsilon}\left\{\frac{\alpha\beta\kappa}{3}\left[2\tau(\kappa R) + \frac{\alpha}{2}C'\sigma(\kappa R)\right] - \left[\frac{6\alpha\beta}{5R} - \frac{1}{\delta_1}\left(\frac{1}{2} + \frac{Z}{P}\right)\right] + \frac{\beta\kappa}{3}\left[\tau(\kappa\delta_1) + \frac{\alpha C'}{2}\sigma(\kappa\delta_1)\right] + \frac{n_s\beta C'\kappa}{3n_p}\sigma(\kappa\delta_2)\right. \tag{3-4}$$

where

$$\beta = 1 - 2Z/P \quad \text{and} \quad C' = \frac{n_p(2\alpha m_p^- + m_p^+ - n_p \alpha v_p^+)}{n_p \alpha^2 m_p^- + n_p \alpha m_p^+ + 2n_s m_s} .$$

Combining the observed value of ΔF_e and (3-4), the radius of macro-ion, R, can be estimated, with stoichiometric number of charges, Z, independent of the polymer concentration. In Table 3, the results obtained are shown, using the experimental data described in § 2 of this chapter and numerical values of $pK_o = 2.50$, $\delta_1 = 5A.$, $\epsilon = 80$, $T = 298^\circ K$. The assumption is also made of the constancy of the observed pK values over the polymer concentration range covered, even at extreme dilution.

Table 3. Radii of PVAG Estimated from Titration Data*

sample	P	S	C_p	R(A.)
S-C	970	10.80	4	57
			2	66
			1	72
			0	240
S-8	1700	3,46	7	61
			4	65
			0	210
S-2	890	2.55	8	39
			4	46
			2	51
			0	90
S-5	370	2.97	7	26
			4	29
			0	40

* $\alpha'' = 0.5$, salt-free, $T = 298^\circ K$.

R at extreme dilution is found to be of the order comparable to the half value of the root mean square end-to-end distance determined from the limiting viscosity number (obtained by the Fuoss plot) using the Flory-Fox equation.[44] Comparing the magnitudes of R of S-8, S-2 and S-5 at the same finite concentration, we notice a proportionality between R and a square root of P. This is not inconsistent with our spherical model at the beginning, and shows that the observed insensitivity of the titration curve of polyelectrolytes, i.e., ΔF_e, to the degree of polymerization is only apparent. (The proportionality does not hold at extreme dilution: this may be due to errors in the assumption of the constancy of pK and due to imperfections of our treatment which were noted in Chapt. 2.)

As is readily seen from Table 3, with increasing polymer concentration R decreases rapidly at first, and then more slowly, reaching a limiting value. This tendency is also obtained when use is made of the titration data of poly(methacrylic acid) by Oth and Doty.[45] In the high polymer concentration range, the macro-ion may be expected to be curled up to nearly the same extent as the neutral polymer, or possibly less. The radius of the coil of a parent PVA molecule in aqueous solution is estimated to be 105 (P =1820), 77 (P = 1035) and 43A. (P= 360) when the viscosity equation of Einstein is used.[46] (Use of the Debye-Bueche relation, with the shielding ratio = 8,

leads to a little higher value of the radius.) This indicates that our estimates of R are of reasonable order.

The concentration variation of R invites some comments. It has been established that the reduced viscosities of polyelectrolyte solutions have a characteristic dependence on the polymer concentration. Only a qualitative statement was made previously by Fuoss[47]: with increasing concentration, the number of counter-ion fixed inside the polymer domain increases to decrease the electrostatic interaction between the ionized groups and cause the macro-ion to shrink. According to Wall et al., the fraction, as was referred to before, was shown to be almost independent of the polymer concentration and applied field intensity.[48] These results seem to contradict Fuoss' interpretation. We are in a position to give an alternative interpretation in conformity with the concentration dependence of R listed in Table 3, which indicates that it is highly probable that the molecular extension is determined mainly (1) by the inter-macro-ion interaction and (2) by the intra-macro-ion interaction in dilute solution. The first factor is most likely to oppose the expansion, while the second would operate to dilate the macro-ion as generally accepted. The former is possibly predominant in the dilute concentration range, but it would cease to be so with diminition of the concentration. (When the volume effect of macro-ions becomes very large with increasing polymer concentration, according to the definition

of $\varkappa$, (2-11), the apparent ideality of the soltuion is approached again. Therefore this statement can not be correct in higher concentration ranges.) Thus the polymer expands. Further dilution makes the second take the place of the first. In such a concentration range, the macro-ion would be extended to its maximum dilation depending on the elastic factor of the chain and so on, and though not necessarily fully stretched, the dilation would be nearly constant with changing concentration. (The value of R decreases steadily with concentration in Table 3, which disagrees with our present assertion. This seems due to lack of titration data at higher dilution.) This variation of extension in wide concentration range may be well reflected in the reduced viscosity curve: $\eta sp/C_p$ increases with decreasing concentration and, exhibiting a maximum value at a concentration that would be supposed to be strikingly low of the prevailing interionic interaction, suddenly drops. The appearance of this maximum has been confirmed by some authors.[49-54] Addition of simple electrolytes would cause lowering of the inter-macro-ion interaction, which helped us to find the maximum at higher concentration with facility.[49,50, 52-55]

It must be mentioned that the nearest neighbour interaction was neglected here. We believe that this interaction would become significant when the concentration of added salt is sufficiently high.[56]

§ 4. Salt Concentration and Temperature Dependences of Extension of Macro-Ion

From the procedure outlined above, we can estimate the extension of a macro-ion at various concentrations of foreign salt and at various temperatures. The dependences of titration curve on these two factors will be treated in this section, with an aim to manifest the validity of our treatment once again.

(A) Effect of Salt Concentration. Gregor and Frederick have reported the experimental study on the titration behaviours of poly(acrylic acid) in the presence of foreign salt.[57] The results show that the polyacid becomes strong when the salt concentration increases. With their results, we obtain the values of R using (3-4) and numerical values of $pK_o = 4.25$,[58] $\delta_1 = \delta_2 = 5$A. and P = 2000.[59] The calculated values are shown in Table 4, and are in the trend usually accepted that the macro-ion shrinks up with increasing salt concentration. (More systematic study will be described in Chapt. 4.) It

Table 4. Salt Concn. Dependence of Radius of PAA Estimated from Titration Data*

KCl (M)	R (A.)
0	70
0.01	65
0.1	40

*polymer concn.=0.01 base mole/l., $\alpha' = 0.1$, T = 298°K.

has to be mentioned that Tables 3 and 4 indicate that the rise of the salt concentration could have qualitatively the same effect as that of the polymer concentration on the molecular extension. This equivalency has been well-established by viscometric evidence and is assumed implicitly at the beginning of our treatment.

(B) Effect of Temperature. Potentiometric titration of polyelectrolytes was not studied at various temperatures. We performed the study at the temperatures of 10, 30 and 60° ± 0.5°C using PVAG, with a pH-meter (M-3 Type) of Horiba Instruments Inc. The reproducibility of the data was 0.05 pH unit. The apparent dissociation constant, K, of PVAG was determined with use of (3-2) and is shown in Table 5. As is readily seen, the values of pK become larger as the temperature increases. It has been reported[58] that the dissociation constants of a number of weak simple acids exhibit maxima between 0 and 60°C, and, exceptionally the value of fairly strong acid like monochloroacetic acid increases steadily with temperature. When compared with these observations, the result shown in Table 5 is not characteristic of PVAG except that the increase of pK is steeper than the cases of low molecular acids.

In order to evaluate the variation of the molecular extension with temperature, the intrinsic dissociation constant, K_o, has to be known with its coefficient of temperature depen-

Table 5. Temperature Variation of pK of PVAG*

temp. (°C)	10	30	60
pK	2.6	2.9	3.2

*sample: SI-1(P = 2150, S = 7.05 mol.%)
C_p = 1.49 g./l.

Table 6. Estimated pK_o of PVAG

temp. (°C)	10	25	30	60
pK_o	2.4_5	2.5_0	2.5_1	2.6_3

dence. The coefficient for our material is provisionally assumed to be the same as that of the dissociation constant of monochloroacetic acid. Then we can obtain pK_o values of PVAG at various temperatures with pK_o = 2.50 at 25°C, which are tabulated in Table 6.

Thus we are able to determine, from the observed pK (Table 5) and pK_o (Table 6), the molecular extension of PVAG using (3-4) and ϵ = 84, 78 and 67 for 10, 30 and 60°C respectively. The results are illustrated in Table 7, which indicates that R decreases with increasing temperature at a fixed polymer concentration.

If such an effect of temperature on the molecular extension well reflects the real state of affairs, the correspond-

Table 7. Radius of PVAG as a Function of Temperature Estimated from the Titration Data*

C_p (g./l.)	R (A.)		
	10 (°C)	30	60
6	76	62	43
2.5	100	70	64
1.0	114	83	74

*The estimation was carried out using the values of P = 1700 (not 2150), and pH at $\alpha'' = 0.5$ of SI-1 (i.e., pK in Table 5). Because the titration curve does not depnd on P, and because S of SI-1 is nearly twice as large as that of S-8, the radius shown herein corresponds approximately to the radius at $\alpha'' = 1$ of S-8 employed in the viscosity measurements (Fig. 6).

ing shift of the reduced viscosity with temperature should be expected to occur. The viscosity of one sample of PVAG was measured at the three temperatures (± 0.1°C) using an Ostwald viscosimeter, which had the following characteristics: capillary radius, 0.343 mm.; volume of bulb, 1.80 cc.; length of capillary, 14.6 cm.; maximum head drop, 4.8 cm.; efflux time for twice distilled water, 132.1 sec (30 ± 0.1°C). The kinetic energy correction was negligible. To avoid marked influence of a trace of ionic impurities on the viscosity data, the glass vessel employed was steam-washed before the solutions were prepared.

The result of viscosity measurement is shown in Fig. 6.

The tendency that the reduced viscosity falls with increasing temperature is in accord with observations by Mock and Marshall[59] and Inagaki et al.[55] It is of importance to make mention of the agreement with the temperature-variation of the above calculated radius.

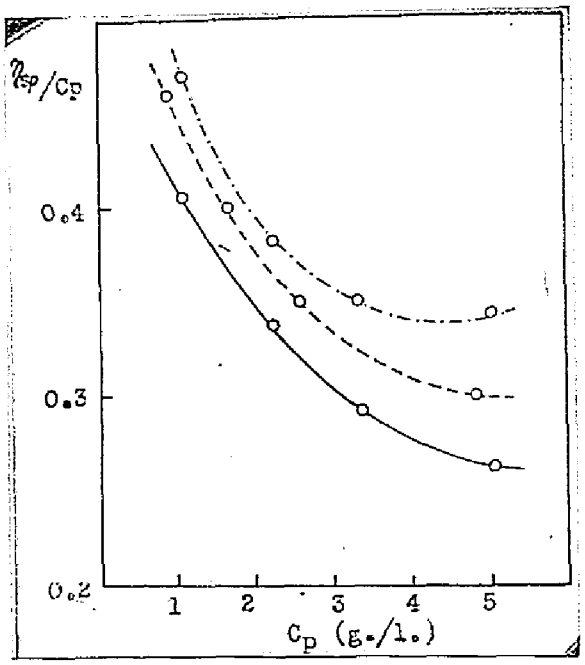


Fig. 6. Reduced viscosity curves of PVAG at 10 (-·-·-), 30 (----), and 60°C (——).

The effect of temperature on the viscosity of neutral polymer solutions had been examined by some investigators. As previously reviewed by Sakurada and Bawn,[60] on raising the temperature, in good solvents the dominating attraction between polymer and solvent is reduced and the polymer is then curled up whereas in poor solvents the attraction between submolecules of polymer is diminished by increased thermal motion and the polymer chains uncurl. Accordingly, lowering or rising of the reduced viscosity with temperature will be observed according as the solutions are formed exothermically or endo-

thermically. The experiments on PVAG indicate the same behaviour as that of neutral polymers in good solvents. Needless to say, the repulsive force between ionized groups supersedes the attraction between solvent and polymer, and the interionic interaction has to be taken into consideration.

If the molecular extension were determined by the intra-macro-ion interaction only, the polymer coil would dilate with rising temperature, because the repulsive force between ionized groups becomes prevailing due to the decrease in dielectric constant of water. This is clearly contradictory to the experimental evidence. Contrary to the effect of the intra-macro-ion interaction, the inter-macro-ion interaction which, as we stressed in Chapt. 2, has been neglected in most of the theories of polyelectrolyte solutions previously published, seems to cause a decrease in the molecular extension. This kind of interaction becomes influential as temperature rises, owing to the same reason as in the case of intra-macro-ion interaction. Therefore it can be said that observed variation of the viscosity of polyelectrolyte solutions with temperature is a further evidence to manifest the importance of the inter-macro-ion interaction.

§ 5. Discussion

It may be useful at this point to mention the physical basis from which the molecular extension can be deduced.

With all other conditions fixed, the electrostatic potential inside the macro-ion is determined by the extension: the potential will be decreased as the polymer chains uncurl. The average dissociation constant corresponds to the work required to bring a hydrogen ion from inside the field of this (extension-dependent) potential to infinity. Therefore the titration curve depends on the extension.

This dependence appears to contradict the usually observed insensitivity of the titration data towards the degree of polymerization, P. It must be borne in mind that the potential is determined by the total number of charges on the polymer chain and by the extension, both of which are dependent on P: with increasing P, the total number increases proportionally to P and the extension also becomes larger. These two factors give rise to an increase and decrease in the potential respectively. Therefore we are led to the conclusion that the insensitivity mentioned above shows partial cancellation of these two effects.

The effect of counter-ion size upon titration behaviour of polyelectrolytes has been studied by Gregor et al.[57,61] who found that polyacids became progressively weaker with increasing size of the counter-ions. This phenomenon was interpreted by them to show that polyions fixed a number of counter-ions in close proximity to the chain, and a theoretical interpretation was given using a rod-like model. This model, how-

ever, does not seem valid to us, especially in the non-extreme dilution. On the other hand, (3-4) giving an expression for ΔF_e shows that ΔF_e (hence pK) increases with increasing δ_1, a parameter dependent on the size of counter-ion, when R is fixed. This trend is certainly in accord with the experiment. Because of lack of the data at low degrees of neutralization, only to which our treatment is accessible, the quantitative discussion can not be developed. However, it can be said that no specific chemical explanation needs to be introduced at least so far as the experimental evidence accumulated up to the present is concerned.

In this chapter, it is made clear that our treatment can provide a fairly satisfactory picture of the complicated behavious of polyelectrolyte solutions, and the titration curve is a powerful source of information on the molecular extension. Regretfully, we are not in a position to quantitatively examine the magnitude of R in the non-extremely dilutions, because no convincing information has not yet been obtained from other approach at present, We believe, however, that the decrease of R with concentrations of polymer and foreign salt and with temperature would be so close to reality. Therefore we can step in the following consideration on the viscosity of polyelectrolyte solutions and on the definition of the "ionic strength".

Note. The correction contained in (3-2) was independently considered by Eisenberg (See Ref. 101).

CHAPTER 4

VOSCOSITY OF DILUTE SOLUTIONS OF POLYELECTROLYTES

§ 1. Introduction

It has been well-established that the reduced viscosity of dilute solutions of polyelectrolytes shows the remarkably different concentration dependence from that of neutral polymer solutions. It is observed to increase so steeply with decreasing concentration in the salt-free solutions that the limiting viscosity number $[\eta]$ can not be determined with high accuracy.

The proposed methods of extrapolation for determining $[\eta]$ can be classified into two groups. First of them is a method of Fuoss and Strauss[62] that utilizes a linear relation between the reduced viscosity, η_{sp}/C_p, and the square root of polymer concentration, $C_p^{1/2}$. As pointed out recently by many authors, however, the $\eta_{sp}/C_p - C_p$ curve has a distinct maximum at a very low concentration,[49-54] so that this method of extrapolation seems definitely dubious. The second method, on the contrary to the first which employed an empirical relation, is based on the choice of a parameter by which the experimental data can be rearranged so that the linearity between η_{sp}/C_p and C_p can be secured. (The detailed discussion was given by Terayama and Wall[63] on these methods of extrapolation.) Some parameters were chosen, which can be distinguished by their

physical significance to each other. However not all of them have an unlimited validity and can give the linear relation desired. The method of dilution proposed by Pals and Hermans[64] is of interest in some respect: though the original intention to determine $[\eta]$ in salt-free solutions was not satisfactorily attained, the method seems to contain useful suggestions for interpretation of the concentration dependence of viscosity. In this chapter, attention will be focused on this method of dilution, and some analysis will be given.

§ 2. Preliminary Considerations

Pals and Hermans (P-H) have defined a quantity, X_o, which was called by the name of "effective ionic strength" for polyelectrolyte solutions. This is clearly an extension of "ionic strength" for simple electrolyte solutions. According to them, X_o is related to the concentration of foreign salt (mol./l.), X, the concentration of polymer (g./l.), C_p, and the number of equivalents per gram of the polymer, δ, by the relation

$$X_o = X + \delta C_p m, \qquad (4\text{-}1)$$

where m denotes the number of moles of foreign salt which is required to replace one equivalent of the polyelectrolyte. The method of dilution is to determine the parameter m so as to obtain the straight $\eta sp/C_p - C_p$ line, keeping X_o constant.

It is noteworthy that the first term in (4-1) reduces to

the usual "ionic strength" when the foreign salt is of 1-1 type and the second expresses polymer concentration effects. Apart from the arbitrariness in determining the value of m, it is of great significance that these effects were introduced into a parameter chosen for description of the polyelectrolyte solutions. We mentioned in Chapt. 2 that theories or interpretations on the solutions previously published have not considered the presence of more than one macro-ion with a few exceptions. This omission has made the treatments unnecessarily intricate and has led the theories to the failure in giving an interpretation, from a unified stand-point, regarding many varieties of properties. Whether the "effective ionic strength", defined on the ground of the assumption of an equivalency of simple and polymeric electrolytes, is a characteristic quantity for the polyelectrolyte solutions, just as the "ionic strength" for simple electrolyte solutions, will be determined by the physical implication of the parameter m.

The linear relation between $\eta sp/C_p$ and C_p, from which m can be determined, has been found out originally for the neutral polymer solutions. It can be approximately admitted that the extension of the polymer is kept constant on this line. From an analogy of the situation, we could expect that the extension of a macro-ion on the P-H dilution line is independent of concentrations of polymer and foreign salt. We will, in the following consideration, regard this expectation as a cri-

terion for judging validity of the treatment employed with a purpose of exploring the character of m.

§ 3. Experimental

(A) Material. The material used is again poly(vinyl alcohol) partially acetalized with glyoxylic acid (PVAG).

(B) Viscosity Measurements. The viscosity measurements were carried out at 30 ± 0.1°C with an Ostwald viscosimeter, the characteristic of which was described in Chapt. 3. Potassium chloride was chosen as a foreign salt.

The results of the measurements are given in Fig. 7. The full curves denote the reduced viscosity curves. As is usually the case, the reduced viscosity increases sharply with decreasing C_p for the salt-free solution, i.e. X = 0. (A distinct maximum mentioned in Chapt. 3 was not observed for this material, but it was found out at about 1 g./l. for S-5 (P = 370, S = 2.97 mol. %). According to other reports, the concentration exhibiting the maximum reduced viscosity is much lower than ours. This discrepancy may be due to difference in the charge density of the material used.) As X becomes greater, $\eta sp/C_p$ decreases and the linearity is approached. Though the viscosity of aqueous solution of the parent PVA is, as is expected, strikingly low, it must be mentioned that this low viscosity is exhibited by a PVAG solution which contains a large amount of foreign salt (X = 1). This appears to mean

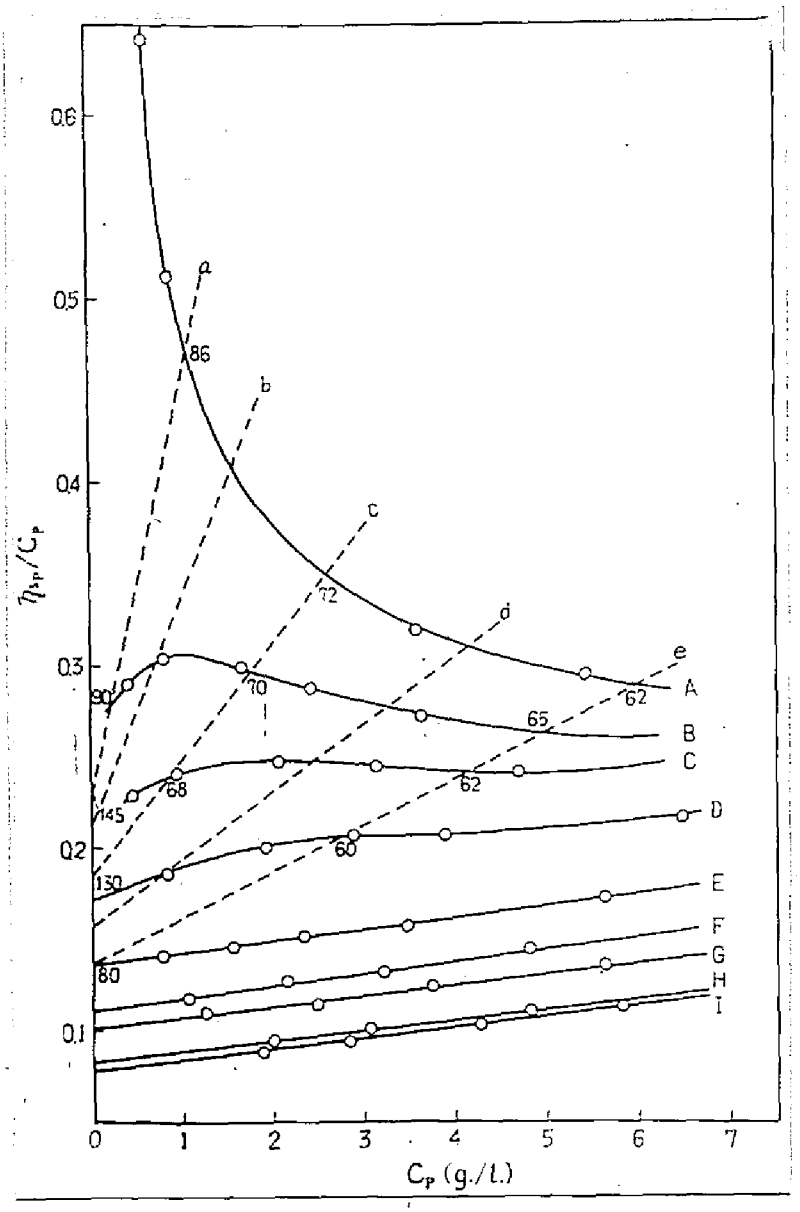


Fig. 7. Observed Reduced Viscosity-Concentration Curves of PVAG in Solutions of Simple Electrolyte and the Pals-Hermans Dilution Lines. (The numerical figures denote the radius of the polymer sphere estimated from titration data.)

Sample: S-8 (P = 1700, S = 3.46 mol.%)
Added Salt: KCl

observed curve	X x 10^3 (mol./l.)
A	0
B	1.25
C	2.5
D	5
E	10
F	50
G	100
H	*
I	1000

dilution line **	X_o x 10^3
a	1.7
b	2.5
c	4.2
d	6.7
e	10

*parent PVA aq. solution

** m = 2.3

that the linearity can not be at once interpreted as an indication of disappearance of electrostatic interaction.

Applying the P-H method of dilution to our observation, we obtain a group of dilution lines (dashed lines in Fig.7) at m = 2.3. According to (4-1), $X = X_o$ holds when $C_p = 0$. Therefore, the intercept on the ordinate gives $[\eta]$ at the concentration of foreign salt = X.

The same measurements were carried out for other two materials and the dilution method was also applied. The values of m are shown in Table 8, with characteristics of the materials. This table indicates that m depends on the degree of polymerization and the charge density. It has been reported that Pals and Hermans obtained m = 1.0 for sodium carboxymethylcellulose, 1.5 for sodium pectinate and 1.0 for chitosan. As m denotes an apparent valency of an ionized group, it might be expected to be unity in our case if the counter-ion fixation is negligible. Before asserting that this value has a sound and reasonable basis, however, the detailed discussion has to be given on the electrostatic interaction, in the field of which the ionized groups are constrained.

Table 8. Observed m-Values of PVAG

sample	P	S	m
SI-2	1420	9.46	1.0
S-8	1700	3.46	2.3
S-5	370	2.97	1.0

(C) Potentiometric Titration. As stated in § 2 of this chapter, we have to obtain information regarding the extension of a macro-ion on the dilution line. For this purpose, a method using potentiometric titration data is employed here again, because no other methods are available at present.

The experimental procedure is the same as the one described in § 2 of Chapt.3, except that a pH-meter of M-3 Type of Horiba Instruments Inc. was used and the temperature of PVAG-KCl solutions was controlled to 30 ± 0.5°C. An example of the salt concentration dependence of the dissociation exponent of PVAG is shown in Table 9, which shows that the presence of foreign salt does not practically affect the pK. This is in contradiction with Katchalsky and Spitnik's and others' observations[65] for poly(acrylic acid) and poly(methacrylic acid). The discrepancy appears to be due to difference in the charge density.

§ 4. Extension of Macro-Ion on the P-H Dilution Line and the Related Problem

(A) Extension of Macro-Ion on the P-H Dilution Line. From the titration data and (3-4), we can estimate the extension of a macro-ion at arbitrary concentrations of polymer and of added salt. The results obtained by this calculation are inserted in Fig. 7. The figures at the intersecting points of observed viscosity curves and artificial dilution lines denote the

Table 9. pK of PVAG as a Function of Concentration of Foreign Salt

Sample: SI-1 (P = 2150, S = 7.05 mol.%)

X (mol./l.)	C_p	pK
0	1.49	3.0
0.011	1.40	3.0
0.103	1.47	3.1
0	2.98	3.0
0.013	2.90	3.0

radius (R) of the spherical macro-ion expressed in A. Here again $pK_o = 2.50$ was used.

It will be realized that the calculated value of R is nearly constant on a dilution line. (Deviation at $C_p = 0$ from the constancy will be discussed later.) This is an interesting result, which agrees with an idea suggested by Pals and Hermans. Since this idea seems to be sound at present, the agreement is considered to confirm that a fundamental postulate involved in our method for estimating the extension is equivalent to that underlying the P-H method of dilution and, at the same time, to assure the correctness of the postulate, which is on an equivalency of simple and polymeric ions. This equivalency manifests itself in the viscosity behaviour: an increase in both salt- and polymer-concentration gives rise to a decrease of reduced viscosity. The P-H method can be said to be nothing but an effort to inquiry the equivalency quantitatively on the ground of this experimental fact.

Reservation has to be voiced concerning the values of R

at $C_p = 0$. We should like to mention some dubious points involved in the calculation. Firstly, care must be taken of the use (at $C_p = 0$) of pK-value which was practically constant over a range of finite concentrations covered. Because of tremendous difficulties encountered in performing the titration at high dilutions, the uncertainty can not be removed. Secondly, there remains a possibility that the error in our treatment used for the present calculation might be fairly considerable at extreme dilution. As was mentioned in Chapt. 2, a model, similar to that of Hermans and Overbeek, was adopted for a macro-ion and a distribution formula proposed by Wicke and Eigen was assumed. Our mathematical expression naturally reduces to that obtained originally by H-O, when the polymer concentration becomes extremely low. Therefore, if any disagreement or contradiction with experiment was found out, it can be ascribed to imperfections of the H-O model; the W-E theory simplifies to the D-H theory which is regarded as a true law in the limit of high dilutions, whereas analysis of approximations inherent to the H-O theory is not yet extensively undertaken. The less reliability of the values of R at $C_p = o$ can be clearly understood after considering that a spherical model has been adopted for a macro-ion and a proportionality between calculated R and a square root of degree of polymerization does not hold at $C_p = 0$.

From $[\eta]$ at an effective ionic strength, the radius of a macro-ion under this condition assumed as a rigid sphere can

be estimated with use of Einstein's equation. The values calculated are 180, 160 and 130 A. for X_o = 1.7 x 10^{-3} 4.2 x 10^{-3} and 10^{-2} respectively, about twice larger than R obtained above at $C_p \neq 0$. This discrepancy may come from the omission of the electroviscous effect in Einstein's theory. As easily expected, taking this effect into consideration would result a smaller radius.

(B) Consideration on m. As mentioned above, m was introduced as a parameter denoting an equivalency of the charge of ionized group and that of simple ion. In our case, the ionized group carries monovalent charge just the ions of foreign salt used. Therefore m = 1 can be taken for granted most naively. Experimentally, however, we have a value other than unity sometimes, as stated above. Stoichiometric consideration, thus, is supposed not to be apllicable: the deviation from unity appears to mean that the charge of ionized group and that of simple ion can not electrochemically have an effect equivalent to the analytical valency. It is not absurd to ascribe this to the electrostatic interaction by which the ionized groups and simple ions are always influenced.

This interaction can be measured in terms of activity coefficient of the solute (or the solvent). It is evident that the choice of a standard state common to polymeric and simple electrolytes is necessary and convenient for further discus-

sion of the present problem. As such a standard state, the ideal state of simple electrolyte solutions should be chosen. It is, here, to be reminded that our activity coefficient calculated in Chapt. 2 is really based on this state. Accordingly, for interpreting the character of m, it will be useful to compare m with $\gamma_{p\pm} / \gamma_{s\pm}$, where $\gamma_{P\pm}$ denotes the mean activity coefficient of polyelectrolytes and $\gamma_{S\pm}$ that of foreign salts.

$\gamma_{P\pm}$ can be formulated using (2-18) and (2-19) and $\gamma_{S\pm}$ is given from (2-16) by

$$kT \log \gamma_{S\pm} = - \frac{e_o^2 \kappa}{3 \epsilon} \left[\frac{n_p \alpha^2 \sigma(\kappa R) + n_p \alpha \sigma(\kappa \delta_1) + 2 n_s \sigma(\kappa \delta_2)}{\alpha n_p (\alpha m_p^- + m_p^+) + 2 n_s} + \right.$$

$$\left. 2 \tau(\kappa \delta_2) \right] . \qquad (4-2)$$

Using the value of R inserted in Fig. 7, $\gamma_{P\pm}$, $\gamma_{S\pm}$ and the ratio can be evaluated for a sample, S-8. The results are tabulated in Table 10, from which $\gamma_{P\pm}/\gamma_{S\pm}$ is seen to be about 1.6 (compare with m = 2.3) except when $X_o = 1.7 \times 10^{-3}$ and $C_p = 0$. It will be noticed that, at $C_p = 0$ calculated value of $\gamma_{P\pm}/\gamma_{S\pm}$ takes a considerably small value for all X_o's when use is made of the value of R shown in Fig. 7. This ratio, however, becomes greater, approaching to 1.6, when the value of R obtained at $C_p \neq 0$ is used, for example 70 A. for $X_o = 4.2 \times 10^{-3}$. This appears to support the less reliability of R at $C_p = 0$ mentioned above. When the estimate of the ratio at $X_o = 1.7 \times 10^{-3}$ is evaluated, the experimental difficulties in the vis-

cosity measurement at such a high dilution has to be taken into consideration. Thus it can be supposed that the parameter m might be giving the ratio of activity coefficient of polyelectrolyte to that of simple electrolyte. This supposition, while not so firm at present, can be examined by direct measurement of the mean activity coefficient of polyelectrolyte, which was undertaken firstly by Chadwick and Neale most recently.[31]

Table 10. Mean Activity Coefficients of Polyelectrolyte and Simple Electrolyte on the Dilution Line and the Ratio

Sample: S-8, m = 2.3.

$X_o \times 10^3$	C_p (g./l.)	$X \times 10^3$ (mol./l.)	R (A.)	$\gamma_{P\pm}$	$\gamma_{S\pm}$	$\gamma_{P\pm}/\gamma_{S\pm}$
1.7	1	0	84	1.1	1.0	1.2
	0.25	1.25	90	1.2	0.9	1.3
	0	1.7	145	0.5	0.9	0.6
			(90)	(1.2)	(0.9)	(1.3)
4.2	2.5	0	72	1.2	0.8	1.6
	1.75	1.25	70	1.2	0.8	1.6
	1	2.5	68	1.3	0.8	1.6
	0	4.2	130	0.3	0.9	0.4
			(70)	(1.1)	(0.9)	(1.3)
10	6	0	62	1.2	0.7	1.7
	4.5	2.5	65	1.2	0.7	1.7
	3	5	62	1.1	0.7	1.5
	0	10	80	0.3	0.8	0.4
			(60)	(1.1)	(0.8)	(1.3)

(C) On the Slope of the Dilution Line. According to Huggins, the slope s of the viscosity-concentration curve is related to the so-called Huggins constant, k', by the following relation,

$$s = k'[\eta]^2 \quad . \tag{4-3}$$

k' of the dilution line can be estimated for our three kinds of materials and is plotted against $1/X_0$ in Fig. 8. From this figure, it is realized that (1) k' of the dilution line is much greater than that usually found for neutral polymers, (2) k' increases linearly with decreasing X_0 and (3) all of our materials have the same linearity. The facts, (1) and (2), were observed by Pals and Hermans for sodium carboxymethylcellulose, but the linearity differed from each others in its slope depending on the degree of polymerization and on the charge density. If our experiment is not in fault, it is tempting to conclude that X_0, depending on a characteristic parameter of the polyelectrolyte, i.e., m, has an implicative significance. As X_0

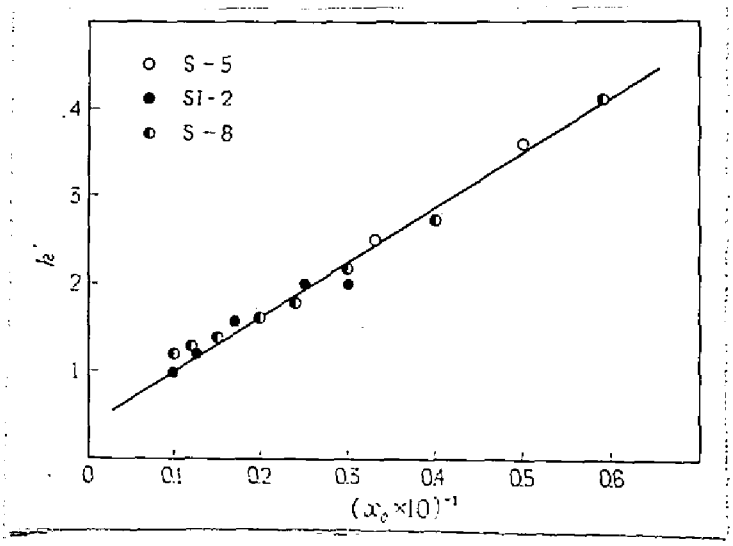


Fig. 8. Variation of the k' constant of the Pals-Hermans dilution line with effective ionic strength, X_0.

becomes greater, we can say, that the solvent power is lowered. If this expression is permitted, the tendency of k' mentioned in (2) is in complete contradiction with the trend of this constant observed for neutral polymers.[66] Our present observation, however, should be interpreted in terms of the surface potential of the macro-ion, which decreases with increasing concentration of foreign salt so that interionic interaction is diminished and k' also becomes smaller. Of course, k' depends also on the segment-density and the flexibility of the chain, which could be neglected in the polyelectrolyte solutions according to our data presented here.

§ 5. Discussion

In the above sections, it was pointed out that the effective ionic strength of polyelectrolyte solutions implicated the physically important significance. So far, it has been introduced and discussed only in connection with the viscosity of the solutions. It is expected that it will be subject to extensive examination in the light of other experimental evidence. Diffusion of the polyelectrolytes might be a pertinent source of informations.

We showed that the parameter, m, was approximately close to the ratio of mean activity coefficients of polyelectrolyte and of simple electrolyte. The variation of m with charge density and degree of polymerization illustrated in Table 8, it

is interesting, can be interpreted at least qualitatively in terms of the dependence of $\gamma_{P\pm}/\gamma_{S\pm}$ with these characters of materials. $\gamma_{S\pm}$, as the numerical calculation shows, is not influenced to an extent, so geat as $\gamma_{P\pm}$, by the characters of macro-ions. Therefore we can omit $\gamma_{S\pm}$ in the following consideration. $\gamma_{P\pm}$ increases with degree of polymerization and charge density, according to (2-18) and (2-19), in the usual case. The charge densities of our materials used here are in the order, S-5 <S-8 <SI-2, and the degree of polymerization increases in the order S-5 <SI-2 <S-8. Since the volume effect on the activity coefficient is much greater than the effect of charge density, $\gamma_{P\pm}$ of S-8 takes the greatest value, as experimentally observed.

It is to be noted that the dilution lines can be distinguished from each others by the extension of a macro-ion, though a value, which is to be determined by the nature of the material, is assigned to m irrespective of the effective ionic strength. The insensitivity of m towards this ionic strength appear, at a first glance, rather curious. It is not clear whether this property of m is able to be observed in a wider range of concentration or not.

CHAPTER 5

ELECTROPHORESIS OF POLYELECTROLYTES

(ONE-COMPONENT SYSTEM)

§ 1. Introduction

Electrophoresis has been an invaluable method to attain a fuller knowledge of behaviours of proteins in solutions. Unfortunately the vast progress in the experimental technique has not been accompanied by a corresponding advancement in the fundamental theoretical interpretation because of structural complexiety of proteins. It is self-evident that useful informations could be obtained if the electrophoretic study is carried out of synthetic polyelectrolytes. Such a study, at the same time, will possibly lead us to a better understanding of the properties of polyelectrolyte solutions themselves.

We will describe our study on electrophoretic behaviours of a polyelectrolyte, poly(vinyl alcohol) partially acetalized with glyoxylic acid, in this chapter. This is a most simplified model of protein, and a compound which was studied extensively by various methods of experiments. The degree of acetalization does not exceed about 20 mol.% and the conclusions presented here might not be valid for the polyelectrolytes of higher charge densities. This restriction, however, would serve to lead us to an understanding of simple and polymeric electrolytes from an unified stand-point, and more importantly, to ex-

amination of an experimental fact obtained recently on poly-(vinyl alcohol), that it migrated towards the anode.

The presence of carboxyl groups on PVA molecules has been pointed out from the polymerization mechanism, and Sakurada and Yoshizaki[67] carried out the conductometric titration to determine the number of acidic groups which was found to be in agreement with that expected from the polymerization mechanism. Sakurada and Hosono,[68] on the other hand, performed the electrophoresis of PVA in simple salt solutions. The number of charges calculated from the mobility was found to be larger than that determined by the conductometry. This has been pointing something to be examined in the method of the calculation, i.e., in the application of Debye-Henry's relation on the electrophoretic behaviour of charged particles. Thus use of a synthetic polyelectrolyte, the number of charges of which can be uniquely determined with high accuracy, will be advantageous for the purpose of examining the theory of electrophoretic migration.

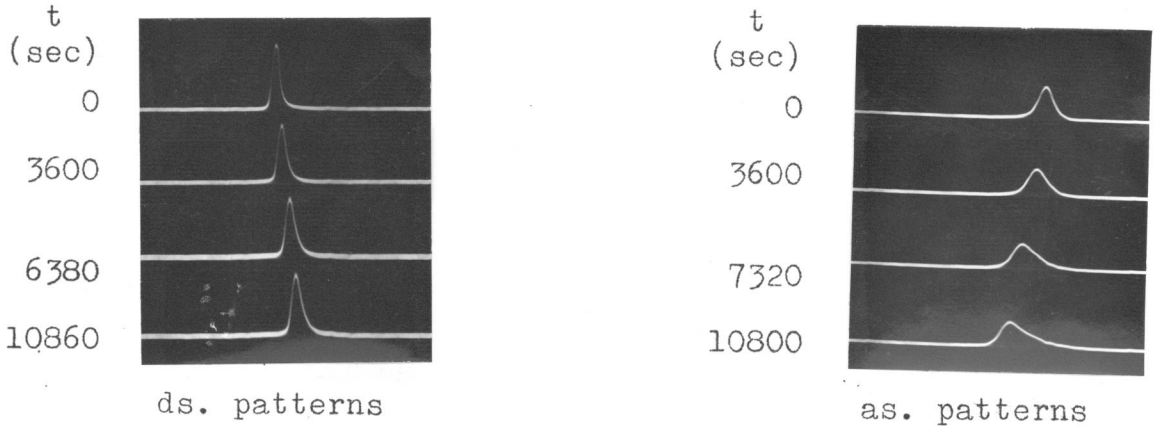
In this chapter, we will deal with the simplest case, that is, one-component system. Attention is focused on the estimation of the number of charges of PVAG by means of Debye-Henry's relation from the mobility and on other related problems.

§ 2. Experimental

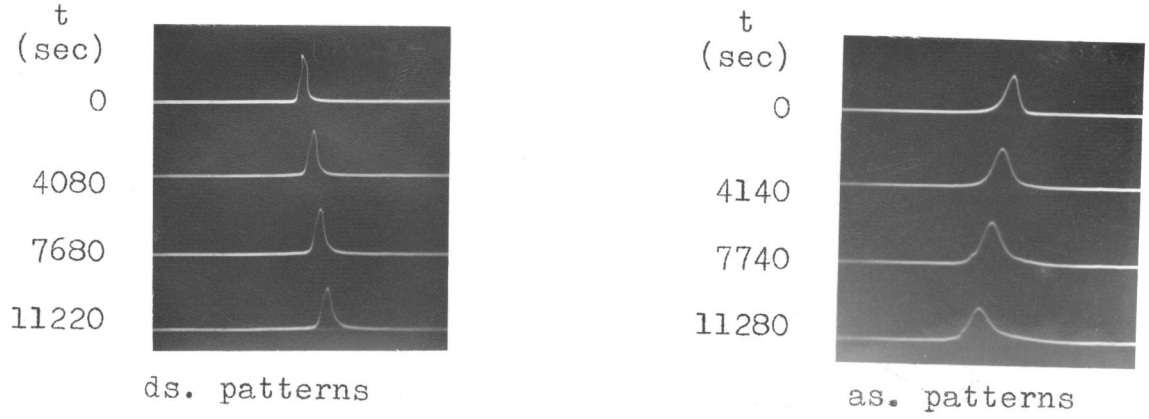
(A) Material. The material used was poly(vinyl alcohol) partially acetalized with glyoxylic acid, (PVAG), that was studied potentiometrically and viscometrically. (See Chapts. 3 and 4.)

(B) Electrophoresis. The electrophoretic mobilities were measured at 15 ± 0.1°C in a Hitachi HT-A Tiselius apparatus by the Schlieren diagonal method. Solutions containing PVAG and the supporting electrolyte were dialysed against large volumes of the supporting electrolye solution against which the boundaries were to be formed. The dialysis was finished when equilibrium indicated by attainment of constant conductance was reached. The concentrations of PVAG were determined by dry weight after dialysis. The electrophoretic current varied from 10 mA to 1 mA, depending on the electrical character of the material and on the conductance of the solution.

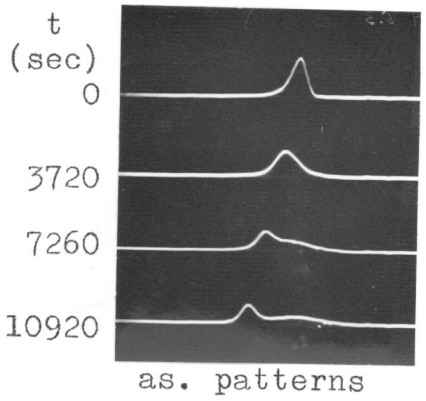
(C) Electrophoretic Pattern and Mobility. Usually the Schlieren patterns of PVAG were symmetrical as Fig. 9 shows, and as many boundaries were observed as the number of ionic species present would account for. In the buffer media of low ionic strengths, stationary epsilon- and delta-boundaries occurred: the lower the ionic strength, the more markedly the delta-boundary becomes. (See Fig. 9.) The displacement of this boundary was not observed in the present experiments.



(A) Sample: S-7, Buffer: CH_3COOK-HCl, μ_s = 0.050, pH = 5.3, C_p = 1.01 g./100 cc., Current = 1.15 mA, E = 0.34 v./cm.

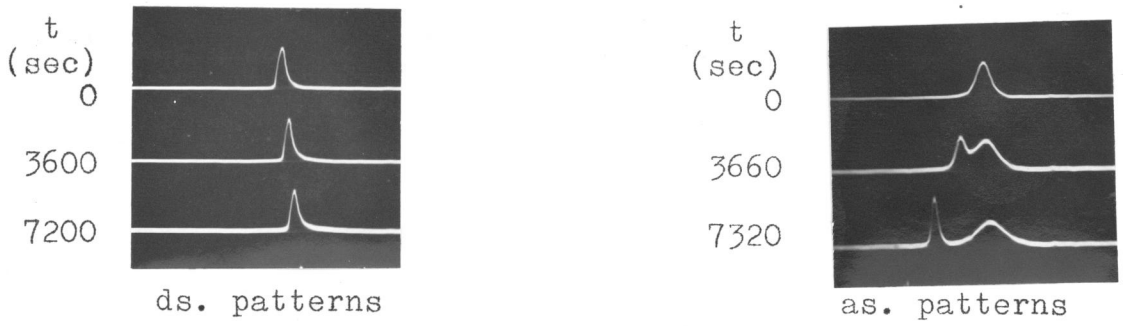


(B) Sample: S-8, Buffer: CH_3COOK-HCl, μ_s = 0.096, pH = 5.3, C_p = 1.52, Current = 5.00, E = 0.86.



(C) Sample: S-8, Buffer: CH_3COOK-HCl, μ_s = 0.028, pH = 5.3, C_p = 0.98, Current = 1.65, E = 0.85.

Fig. 9. Schlieren patterns of PVAG.



(D) Sample: S-8, Buffer: CH_3COOK-HCl, μ_s = 0.009, pH = 5.3
C_p = 1.05, Current = 0.55, E = 0.88.

Fig. 9. (Concluded).

Electrophoretic mobility m was calculated by the relation

$$m = U/E, \qquad (5\text{-}1)$$

where U is the moving velocity of boundary determined from the displacement of the peak of pattern and E the voltage gradient evaluated from the conductivity of the dialised polymer-buffer solution. Practically, U was determined by the displacement (h) of peak in t sec. (In Fig. 10, an example of the h-t relation is given. The slope corresponds to U.) Two mobilities are obtainable from descending and ascending boundaries but the

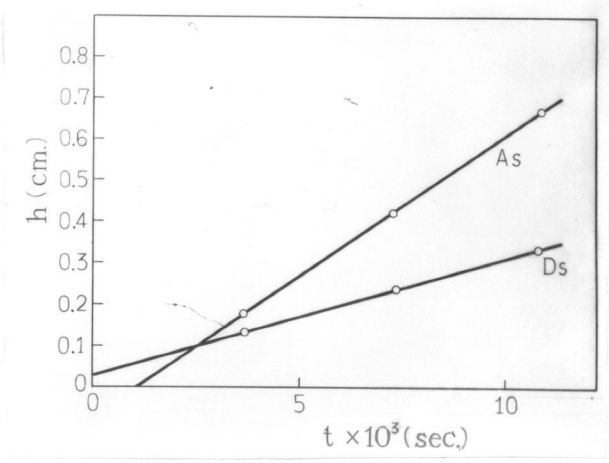


Fig. 10. Displacement and migration time.

quantity in this record refers only to the former. The boundaries traveled towards the anode as expected: the mobility is negative.

§ 3. Experimental Results

(A) Mobility and Degree of Polymerization. Table 11 gives the mobility values obtained with the materials of three different degrees of polymerization (P) and of practically constant carboxyl group content (S). This table shows that the

Table 11. Effect of Degree of Polymerization on Mobility

Buffer: CH_3COOK-HCl, pH = 5.3, μ_s = 0.099,
C_p: ca. 1 g./100 cc.

sample	P	S (mol.%)	m (cm^2 v^{-1} sec^{-1})	R_e (A.)	Q_{tit}	Q_{DH}
S-8	1700	3.46	3.64×10^5	99	59	44
S-2	890	2.52	3.71	68	22	23
S-5	370	2.97	3.23	47	11	11

R_e: radius of a spherical macro-ion estimated by Einstein's theory of viscosity, Q_{tit}, Q_{DH}: number of charges, analytical and calculated.

mobility hardly depends on the degree of polymerization. This is in accordance with the results with PVA by Hosono and Sakurada[68] and with poly(4-vinyl-N-n butyl pyridinium bromide) by Fitzgerald et al.[69] Assuming proportionalities between P and a square of the radius of spherical macro-ion, R^2, and between P and the number of charges on a macro-ion, Q, this independency

can be easily explained by Debye-Henry's relation,[70] which was derived for the virtually rigid sphere,

$$m = f(\chi'R)\, Q/\{6\pi\eta R\,(1 + \chi'R)\}\ , \qquad (5\text{-}2)$$

where $f(\chi'R)$ is the Henry function and χ' the original Debye reciprocal length, since $f(\chi'R)$ is not sensitive to $\chi'R$ and $\chi'R$ is much larger than unity under our experimental conditions. The relation $P \propto R^2$ was originally found for neutral polymers. The viscosity of PVAG used here in the buffer medium, ionic strength = 0.1, does not display the dependence on polymer concentration, which is characteristic of polyelectrolyte solutions, so that it does not seem unreasonable to introduce the proportionality in our case. The proportionality of Q to P can be easily admitted if PVA molecules were uniformly acetalized.

(B) Mobility and pH. The dissociation of polyelectrolytes depends on the pH and the mobility would also depend on the pH. Fig. 11 and Table 12 shows the dependence. For comparative purpose, the titration curves are also indicated. From this figure, it is realized that almost of all acidic groups are ionized at pH $\geq$ 5 and contribute to the electrophoretic motion.

(C) Mobility and Carboxyl Group Content. The mobility values obtained with various carboxyl group content (S) are

Table 12. Effect of pH on Mobility

Sample: S-8 (P = 1700, S = 3.46 mol.%)

Q_{tit} = 59, C_p: ca. 1 g./100 cc.

Buffer: CH_3COOK-HCl, μ_s = 0.096

pH	m x 10^5	R_e (A.)	Q_{DH}
2.00	2.04	95	23
2.42	2.82	96	32
2.72	3.12	96	36
3.10	3.32	97	42
5.30	3.64	99	44
11.40	3.45	108	49

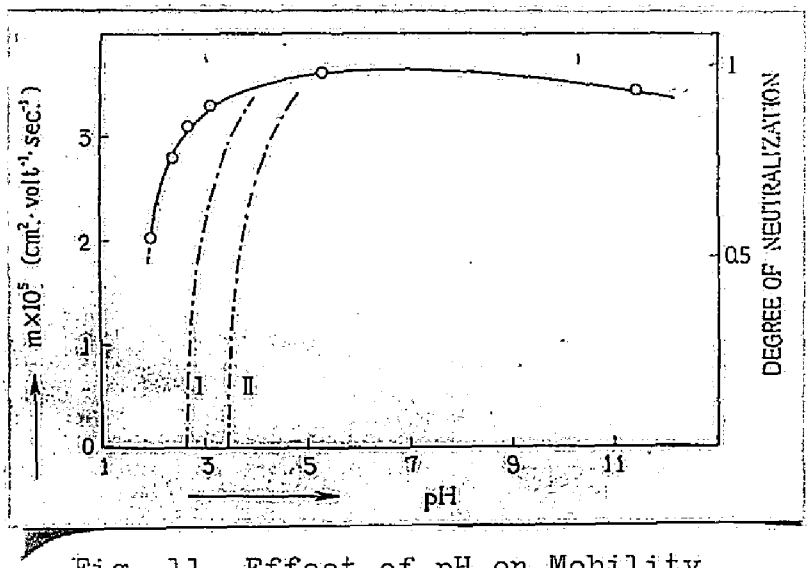


Fig. 11. Effect of pH on Mobility.
Sample: S-8, C_p = 1 g./100 cc. Q_{tit} = 59.
Buffer: CH_3COOK-HCl, μ_s = 0.096.
Titration Curves (μ_s = 0):
I, C_p = 0.69 g./100 cc.
II, C_p = 0.07 g./100 cc.

illustrated in Table 13 and Fig. 12. Interpolation of the mobility to that of PVA (ca. 10^{-5} $cm.^2$ $v.^{-1}$ sec^{-1}) gives the figure of about 0.7 mol.% as the S, which is not so different from the number of charges of PVA previously determined in the buffer of this ionic strength.[68]

(D) Mobility and Polymer Concentration. Fig. 13 presents the mobility against polymer concentration plot. A min-

Table 13. Effect of Carboxyl Group Content on Mobility

Buffer: CH_3COOK-HCl, pH = 5.3; μ_s = 0.099

C_p : ca. 1 g./100 cc.

sample	S (mol.%)	P	m x 10^5	R_e (A.)	Q_{tit}	Q_{DH}
S-C	10.80	970	9.09	102	110	117
S-1	5.73	890	6.80	72	51	47
S-2	2.52	890	3.71	68	22	23

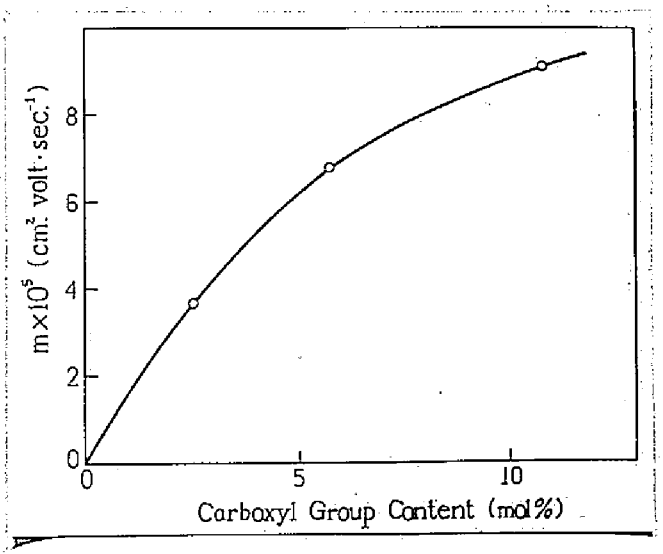


Fig. 12. Effect of carboxyl group content on mobility.

Buffer: CH_3COOK-HCl, pH = 5.3

μ_s = 0.096, C_p: ca. 1 g./100 cc.

imum appears for PVAG of higher carboxyl group contents, which can never be predicted by existing theories and will be successfully interpreted in terms of inter-macro-ion interaction later. Table 14 also represents the concentration dependence.

(E) Mobility and Ionic Strength. Most of the experiments mentioned above were carried out in the buffer solution at a

Table 14. Effect of Polymer Concentration on Mobility

Buffer: CH_3COOK-HCl, pH = 5.3.

(A) Sample: S-7 (P = 1700, S = 5.82 mol.%), R_e = 125 A.
Q_{tit} = 99, μ_s = 0.050.

C_p	m x 10^5	Q_{DH}	Q_{OS}
1.31	9.35	130	78
1.01	8.54	120	71
0.67	7.96	110	67
0.34	8.66	120	72
0	(10.)	(140)	(84)

(B) Sample: S-8 (P = 1700, S = 3.46 mol.%), R_e = 99 A.
Q_{tit} = 59, μ_s = 0.096.

C_p	m x 10^5	Q_{DH}	Q_{OS}
1.52	3.55	43	24
1.14	3.64	44	24
0.86	4.13	50	27
0.50	4.79	58	32
0	(6.50)	(78)	(43)

Q_{OS}: number of charges estimated by means of the Overbeek-Stigter's theory.

range of ionic strength (μ_s) (0.05 - 0.2), which is regarded as appropriate in the case of proteins. The choice of this range is clearly related to the fact that the existing theories on electrophoresis assumed no inter-particle interaction which would become depressed with increasing ionic strength. With a purpose of examining the validity of this assumption, the mo-

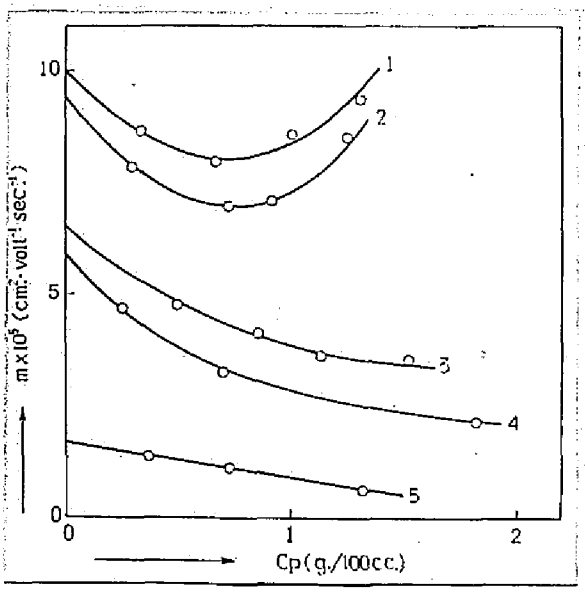


Fig. 13. Effect of polymer concn. on mobility.

curve	sample	P	S	buffer	pH	μ_s
1	S-7	1700	5.82	CH_3COOK-HCl	5.30	0.050
2	S-1	890	5.73	$(COOK)_2$-HCl	3.04	0.097
3	S-8	1700	3.46	CH_3COOK-HCl	5.30	0.096
4	S-2	890	2.52	$(COOK)_2$-HCl	3.04	0.097
5	PVA	890	-	$(COOK)_2$-HCl	3.04	0.097

bility-ionic strength relation was studied. The results are shown in Fig. 14 and Table 15, which indicate that m has a tendency of increasing with decreasing μ_s, as is well explained by Debye-Henry's relation if m is determined predominantly by

Table 15. Effect of Ionic Strength on Mobility

Sample: S-4 (P = 370, S = 6.37 mol.%), Q_{tit} = 24,
Buffer: CH_3COOK-HCl, pH = 6.2.

μ_s	C_p	m x 10^5	Re (A.)	Q_{DH}
0.097	0.37	7.66	43	21
0.049	0.38	8.80	46	25
0.019	0.39	9.43	53	21
0.009	0.37	9.46	60	21

the charges due to ionizations of acidic groups and if R is practically independent of μ_s. In the very low ionic strength range, however, R would increase with decreasing μ_s. According to Debye-Henry's relation, then m could turn to the tendency of decreasing, which was evidently observed with materials of high charge density used by Nagasawa et al.[71]

§ 4. Discussion

(A) Estimation of Number of Charges. Estimation of the number of charges of a charged particle from the electrophoretic mobility (mobility method) has been tried using various proteins by some authors and compared with the values obtained with the aid of other experiments. For example, Overbeek[72] presented comparison of the number of charges by mobility method of ovalbumin with those obtained by membrane potential measurements (membrane potential method) and by titration (analytical method).

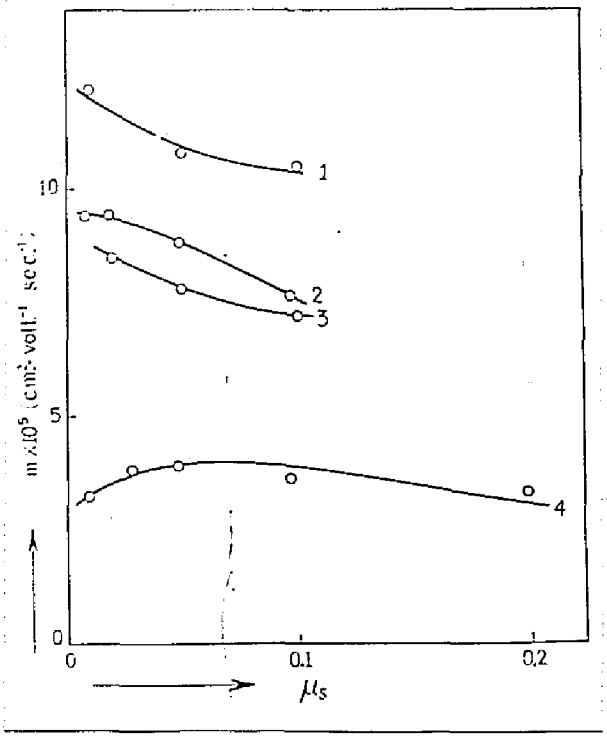


Fig. 14. Effect of ionic strength on mobility.

curve	sample	P	S	C_p	buffer	pH
1	S-10	2150	12.08	0.9	CH_3COONa-NaOH	12.0
2	S-4	370	6.37	0.4	CH_3COONa-NaOH	6.2
3	S-4	370	6.37	0.7	CH_3COONa-NaOH	6.2
4	S-8	1700	3.46	1.0	CH_3COOK-HCl	5.3

According to him, the mobility method rendered the number of charges in good agreement with that obtained by the membrane potential method. However the discrepancy with the results by the analytical method was rather striking, especially when the ionic strength of the buffer is small. This discrepancy, we believe, is due to adsorption of buffer ions by the protein.

the electrophoresis and membrane potential measurements were performed in the phosphate buffer whereas the titration was carried out in the presence of potassium chloride. The adsorption by protein molecules is widely accepted with many kinds of ions except protons and the interaction of protein with phosphate ions is much more remarkable that with chloride ions. Information rendered by titration is clearly regarding the dissociation of protons. Therefore, the above agreement and disagreement are not unexpectable.

Care has to be taken of the assumptions made in derivation of the mobility-number of charges relation, in the above consideration. Examination of the assumptions will be facilitated when use is made of the materials which do not seem to exert a specific influence, like adsorption, on the buffer ions so that the analytical value of number of charges can be taken as most reliable. Synthetic polyelectrolytes are favourable substance. Especially the polyelectrolytes of a relatively low charge density are most appropriate, because those of high charge density would bring about the counter-ion fixation, which makes the problem unnecessarily complicated. We will undertake this examination using the mobility value of PVAG described in the foregoing section. Special mention will be made on the Debye-Henry and Overbeek-Stigter theories.

(1) Number of charges estimated with use of Debye-Henry's

relation. In an attempt to estimate the number of charges on a macro-ion with use of Debye-Henry's relation, attention has to be paid to points that the R values have to be determined independently and the present theories of electrophoresis have dealt with only a single charged particle and Debye-Henry's relation is no exception. Strictly speaking, therefore, the validity is restricted to an extremely dilute solution or a solution which stands in an ideal state so that the mobility value should be preferably extrapolated one to zero concentration, [m] . Q_{DH} estimated with both [m] and R_e determined from the intrinsic viscosity number by the Einstein equation, is shown in Table 16. It does not much diverge from the value

Table 16. Number of Charges of PVAG Estimated from the Intrinsic Mobility

sample	P	S	pH	μ_s	R_e (A.)	Q_{tit}	Q_{DH}	Q_{OS}
S-7	1700	5.82	5.30	0.050	125	99	140	84
S-1	890	5.73	3.04	0.097	86	51	87	52
S-8	1700	3.46	5.30	0.096	99	59	78	43
S-2	890	2.52	3.04	0.097	73	22	40	26
PVA	890	-	3.04	0.097	71	-	11	-

conductometrically determined, Q_{tit}. The disagreement is too small to be attributed to such an adsorption of negatively charged small ions as considered in the case of PVA.[73)]

It is always possible to estimate the number of charges

from the mobility at any finite concentration if we admit its approximate nature. Such estimates were shown in Tables 11 - 15. The R values were determined from $[\eta]$ by means of Einstein's relation and were assumed to be constant in the concentration range in which the electrophoretic runs were observed. The agreement between Q_{tit} and Q_{DH} in those tables suggests, that the extrapolation to the extreme dilution is not always necessary under our experimental conditions. It must be borne in mind that this agreement can not necessarily be expected with materials of high charge density, or in the case that the inter-macro-ion interaction remains prevailing.

However, disagreement is striking between Q_{tit} and Q_{DH} when low ionic strength is chosen. Table 17 indicates that the discrepancy grows while μ_s decreases. The shape factor

Table 17. Number of Charges at Various Ionic Strength

Sample: S-8 (P = 1700, S = 3.46 mol.%), Q_{tit}=59

Buffer: CH_3COOK-HCl, pH = 5.3, C_p: ca. 1 g./100 cc.

μ_s	m x 10^5	R_e (A.)	Q_{DH}	Q_{OS}
0.199	3.50	98	53	25
0.096	3.64	99	44	24
0.048	3.95	104	40	25
0.028	3.82	112	36	25
0.009	3.26	124	24	20

of the macro-ion might immediately come into mind. As already shown in Chapt. 2, however, the shape and size of linear and ideally flexible polyelectrolytes in solutions are considered to be determined by not only the intra-macro-ion interaction, but also the interionic one. In the dilute solutions, the polymer chain can not be deemed to be shrunk or elongated only in a fixed direction: the chain is curled up to be spherical. By this guessing, it would seem rational to attribute the growing discrepancy mentioned above to the interionic interaction which has not been dealt with in Debye-Henry's relation but, in reality, would become predominant as the ionic strength decreases. Taking no account of this interaction really results in an underestimation of the screening parameter, accordingly of the number of charges.

Two comments of general interest should be mentioned. Combining Debye-Henry's relation and Einstein's, some question might rise by lack of any rigorous proof on the equivalency of these two rigid sphere models. However, the use of other theories (for example, Flory-Fox's and Debye-Bueche's) in preference to Einstein's for the present purpose seems no more consistent with Debye-Henry's theory in respect of the model. Secondly it is necessary to consider the possibility of counter-ion fixation. As Wall has shown in an elegant manner,[17] a number of counter-ions travels with the polyions in a region of high degree of neutralization, but only a few are associated

with the polymer coil at a low degree of neutralization. Therefore this kind of association could be presumably out of consideration with materials of a few ionized groups like ours. This could be said to confirm the agreement between Q_{DH} and Q_{tit}.

(2) Number of charges estimated with the use of Overbeek-Stigter's theory. The Debye-Henry theory assumed a hydrodynamically rigid sphere model. It is worthy to question whether the polymer molecules in consideration can be adequately replaced by this model. Therefore it would be interesting to apply Overbeek-Stigter's theory for estimating the number of charges, which assumed the same model for a polymer as Debye and Bueche's theory of viscosity.[75] According to Overbeek and Stigter (O-S), the mobility is given by

$$m = \left\{ (Q_{tit} - Q_{eff})/Pf + Q_{eff}/F - Q_{eff}\kappa' R'/6\pi\eta R'(1+\kappa' R') \right\}, \tag{5-3}$$

where R' is the radius of a macro-ion sphere (estimated from the limiting viscosity number by means of Debye-Bueche's theory), F the frictional constant of the sphere, f the friction factor of one bead, Q_{eff} the number of effective charges and the others were already defined. The shielding ratio σ was to be almost independent of the degree of neutralization α'' when $\alpha'' < 0.1$, by Oth and Doty's experiment on poly(methacrylic acid).[45] Thus for PVAG used here we can take the value of $\sigma = 8$ originally found for PVA. When $\sigma > 5$, the first term of

of the right-hand side of (5-3) becomes negligible and we obtain

$$m = \left\{ Q_{eff}/F - Q_{eff}\varkappa'R'/6\pi\eta R'(1 + \varkappa'R') \right\} . \qquad (5\text{-}4)$$

The number of charges calculated with (5-4) and $\sigma^- = 8$ is denoted by Q_{OS} and is shown in Tables 14, 16 and 17. The agreement at $C_p = 0$ between Q_{OS} and Q_{tit} is satisfactory. However, it might be advisable to use a larger value for σ^- than 8 in the salt-containing systems. (Note that Q_{OS} is always smaller than Q_{tit} as Table 17 shows.)

(3) Related problems. From above considerations, the electrophoretic behaviours of PVAG are seen to be interpreted by Debye-Henry's relation. This clearly supports informations on the number of charges of a PVA molecule. It is to be mentioned that the theory has an advantage that it contains only a single parameter, R, which can be evaluated by another independent method of experiment and at the same time a disadvantage of the omission of inter-particle-interaction, which can be remedied by application of Wicke and Eigen's theory. Taking the inter-particle-interaction into consideration, that is, discussing the mobility as a function of the polymer concentration, was at least qualitatively successfully carried out by Hosono and an appearance of a minimum in the mobility vs. concentration curve (see Fig. 13) was verified. His final expression was

$$m = f(\varkappa R)\ Q/6\pi\eta R(1 + \varkappa R), \qquad (5\text{-}5)$$

and is in formal accordance with (5-2). It should be noted that χ in (5-5) is a screening parameter defined by (2-11). The appearance of a minimum, as in the cases of activity coefficient and osmotic coefficient, has its origin in the volume effect of a macro-ion and in the electrostatic interaction between the macro-ions. The minimum would shift towards a higher concentration with decreasing degree of polymerization and charge density, or with increasing ionic strength. These properties of the mobility-concentration relationship will become important in interpretation of the so-called boundary anomalies, which will be discussed in the next chapter.

An interesting method of calculation of number of charges has to be noted, that was presented by Charlwood.[76] His method was based on the condition of disappearance of epsilon- and delta-boundaries, that the Kohlrausch regulating functions in both sides of the boundary should be equal. This function involves the mobilities of all the ions and their electrochemical equivalents. If the experiments are conducted so as to determine the concentrations of the buffer solutions against which the protein-containing solution has been dialysed and at which the delta-boundary is completely eliminated, we can estimate the protein concentration in terms of electrochemical equivalents and hence the valency. This method of calculation, essentially different from those of Debye-Henry and of Overbeek-Stigter, assumes no geometrical model for the

charged particle. Although the delta-boundary measurements give rather higher values of the valency, the treatment can apply to the cases when knowledge concerning the shape factor is lacking. It is interesting to see that in this method there is a requirement of the Kohlrausch theory that the mobility of a given ion should be independent of its position. In practice, there may be considerable alternation of the mobility of charged particles across the boundaries. Naturally, then, Charlwood's method would fail. We can not use this method for PVAG, because not all necessary informations for the application are available at present. We are regretfully satisfied with only making mention of the significant nature and potentiality.

(B) Comparison of Potentiometric and Electrophoretic Potentials.

Our study was extended to comparison between potentiometric and electrophoretic potentials. The electrophoretic mobility was known to be related to the electrophoretic potential ζ_{ele}, surface potential, by

$$m = K \zeta_{ele} \epsilon / \eta \quad , \qquad (5\text{-}6)$$

which is a geheralized expression of (5-2). On the other hand, the potentiometric potential, which is defined by the relation

$$\partial F_e / \partial Z = e_o \zeta_{pot}, \qquad (5\text{-}7)$$

is described as the potential of field inside the macro-ion,

from which a proton is brought out to infinity. ζ_{pot} may be equal to ζ_{ele} only when the potential inside the macro-ion is independent of the distance from the centre. Otherwise, ζ_{pot} is considered to correspond to an average potential. Therefore these two kinds of potentials can not be expected to have an identical value, against Katchalsky's observation.[43] In Table 18, the observed values of these potentials are compared. The discrepancy exists.

Table 18. Comparison between Potentiometric and Electrophoretic Potentials

sample	$\zeta_{ele.obs.} \times 10^5$ *	$\zeta_{pot.cal.} \times 10^5$ *	$\zeta_{pot.obs.} \times 10^5$ *
S-C	3.6	12	9.9
S-1	2.7	6.2	4.9
S-2	1.5	2.6	3.0
S-8	1.8	4.3	3.9

* in e.s.u.

This can be clearly understood if ζ_{pot} is to be referred to an average potential inside the macro-ion as mentioned. According to (2-13) giving the potential inside the macro-ion, we obtain

$$\zeta_{pot}/\zeta_{ele} = (\kappa R + 4)/3 , \qquad (5\text{-}8)$$

assuming $\zeta_{pot} = \bar{\psi}_2 = \int_0^R \psi_2 dr/R$. In Table 18, (5-8) is checked. All values of $\zeta_{ele.obs}$ were obtained, from the extrapolat-

ed value of observed descending mobilities (at the polymer-concentration of 4 g./l.) to zero ionic strength, by means of (5-2). Using the value of κ and R shown in Table 3 at this concentration, $\zeta_{pot.cal.}$ is calculated from $\zeta_{ele.obs.}$, according to (5-8). $\zeta_{pot.obs.}$, which is evaluated by (5-7) from the observed values of $\partial F_e/\partial Z$, is in a good agreement with $\zeta_{pot.cal.}$. This agreement supports our assumption.

CHAPTER 6

ELECTROPHORESIS OF POLYELECTROLYTES (TWO-COMPONENT SYSTEM)

§ 1. Introduction

In Chapt. 5, the electrophoresis of polyelectrolyte was described and the Debye-Henry theory was shown to well apply to the behaviours of a synthetic polyelectrolyte in its one-component system. In this chapter, we are dealing with two-component systems which are consisted of two kinds of polyelectrolytes. Main interests will be put in the interpretation of boundary anomalies in terms of Dole's theory of moving boundary.[77] This will serve to obtain fundamental knowledge concerning the electrphoretic behaviours of natural protein which usually occurs as a mixture of a number of components and to manifest the limits and imperfections of the theory of moving boundary which furnishes informations of the number of the newly established boundaries, their velocity of displacement and the concentrations of components in the phases developed after passing of an electric current.

The word, "boundary anomalies," is here limited to (1) disagreement between mixing-ratio of two components obtained analytically and that determined from the area of electrophoretic pattern, and (2) appearance of epsilon- and delta-boundaries and their displacements. The experimental evidence

on these boundaries has been abundantly accumulated and many theoretical approach has been proposed. However, attention has been so far principally paid to determination of the experimental conditions to eliminate these boundaries, in other words, to obtain knowledge concerning the ideal conditions for electrophoretic migration. For example, Svensson[78] has theoretically shown that these boundaries, together with other anomalies, disappear when small protein concentration and high ionic strength are chosen.[79] In fact, the experimental result shows that, under these conditions, the boundaries can be eliminated and the Schlieren pattern in the descending channel is the mirror image of that in the ascending channel, and moreover, the mobilities obtained in both channels are identical. However, this limiting or ideal case can not be always approached: lowering of protein concentration would result in an unstable and optically undetectable moving boundaries, and increase in salt concentration would be limited by an upper limit imposed by the apparatus. Therefore, in order to know the ideal behaviours, the extrapolation of observations at finite polymer and salt concentrations is unavoidable to zero polymer concentration or to infinite ionic strength. This extrapolation is usually accompanied with a source of rather crude errors, and it is hoped that it will be removed by establishing interpretation of the anomalies.

For this purpose, our planned course of study will be one

of most useful first step. The material has been examined extensively with various methods of experiments: the results described in Chapt. 5 on the one-component system will be most helpful. We will interpret the above anomalies in terms of electrostatic interaction, which was discussed in Chapt. 2.

§ 2. Experimental

(A) Material. The materials used are poly(vinyl alcohol) partially acetalized with glyoxylic acid (PVAG). The method of preparation and the characteristics were referred to in Chapt. 3. The solutions were prepared by dissolving a weighed amount of two kinds of PVAG into the buffer solutions of CH_3COOK-CH_3COOH (pH = 6.2) and then by dialysing the polymer-containing solutions against the buffer solutions until equilibrium indicated by attainment of constant conductance was reached. The mixing-ratio of two components was determined by the weight-ratio before the dissolving. The concentration was determined by dry weight after dialysis.

(B) Electrophoresis. The experiments were carried out in the same apparatus as mentioned in Chapt. 5.

(C) Determination of Electrophoretic Mobility. The details were given in Chapt. 5. The volume change of the electrode was neglected[80] though the total amount of electricity was higher than that in one-component system. Unless specified,

the displacement of the boundary was determined from the peak of the pattern, and the voltage gradient in the newly established phases was assumed to be equal to that in the original polymer-containing solution (before the migration) and was used to calculate the mobility.

(D) Determination of Area of Schlieren Pattern. Since the separation of boundaries was in many cases incomplete as Fig. 15 shows, Tiselius-Kabat's method[81] was applied.

§ 3. Experimental Results

(A) Mobility and Voltage Gradient. In one-component systems, the voltage gradient was controlled so as to observe displacement of the boundary (in the descending channel) of 3 - 4 mm. for three hours on the photographic plate, depending on the charge density of the material and the composition of the solution. In order to separate boundaries as efficiently as possible, in two-component systems, it is advisable to choose a potential gradient, at least as high as that employed in the study on one-component system of slowly moving component (slow component). Therefore the fastly moving component (fast component) is to migrate in a higher voltage gradient than that in its one-component systems. In order to compare the results obtained in one component systems with those which will be obtained in this chapter, the effect of voltage gradient on the mobility has to be studied at first. The exper-

Table 19. Variation of Mobility with Voltage Gradient Applied

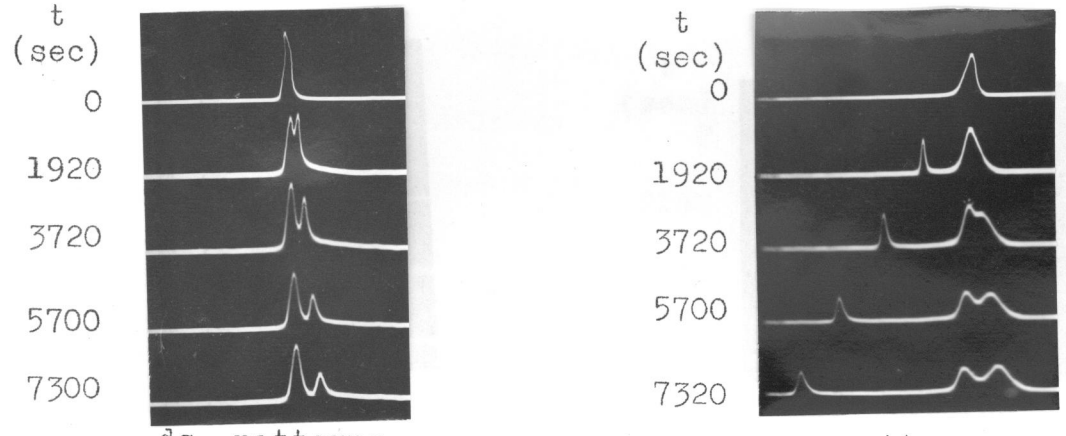
Sample: S-7 (P = 1700, S = 5.82 mol.%)
Buffer: CH_3COOK-CH_3COOH, μ_s = 0.011
pH = 6.2, C_p = 0.66 g./100 cc.

E	$m_{As} \times 10^5$	$m_{Dp} \times 10^5$	$m_{Dm} \times 10^5$	$m_{del} \times 10^5$
2.92	27.1	6.89	12.2	2.14
1.33	27.5	6.86	13.7	2.35
0.34	23.7	9.08	-	0

E; voltage gradient (v. $cm.^{-1}$), m: mobility (the suffix, As, Dp, Dm or del denotes the mobility obtained from the ascending, descending (peak), descending (first moment) or delta-boundary.) in $cm^2\ v^{-1} sec^{-1}$

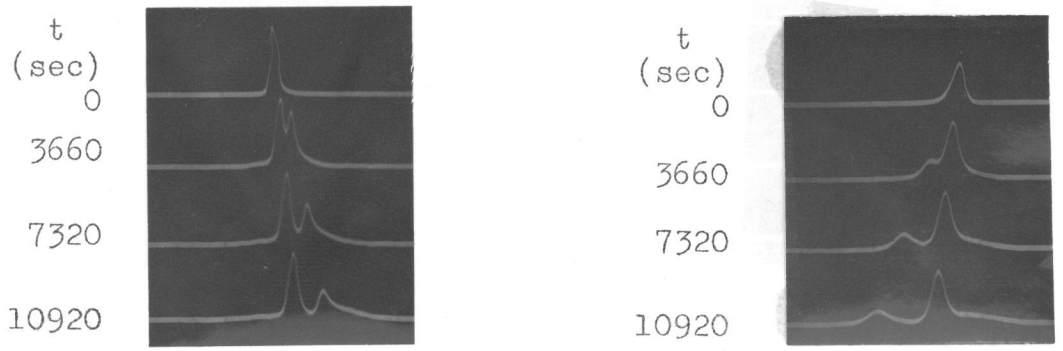
imental results are shown in Table 19. As is seen from Fig. 15, the descending patterns are unsymmetrical at higher voltage gradients. In these cases, the displacement of the peak can not be used for determining the mobility. For considerably unsymmetrical patterns, both the mobility values from the peak and from the first moment of the Schlieren curve were calculated and listed in Table 19. If only the relaxation effect is concerned, m_{Dm} should decrease with increasing E, but this is not the case in our observation. Possibly inhomogeniety of acetalization reaction has to be taken into consideration.

(B) Electrophoretic Patterns and Mobility. The electrophoretic patterns were shown in Fig. 15. In all cases, 2 + 1 = 3



(A) M-2-2.

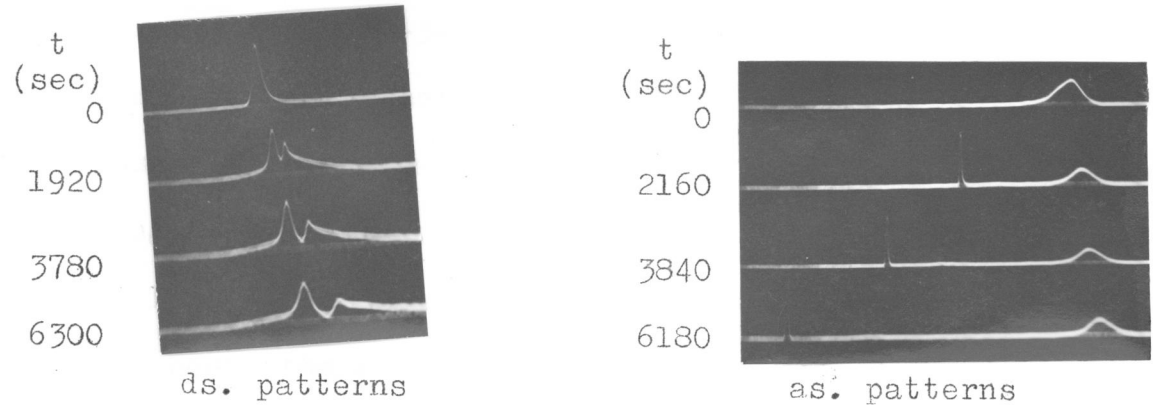
Component 1: PVA (0.83 g./100 cc.)
Component 2: S-2 (0.82 g./100 cc.)
E = 3.03 v./cm., μ_s = 0.011.



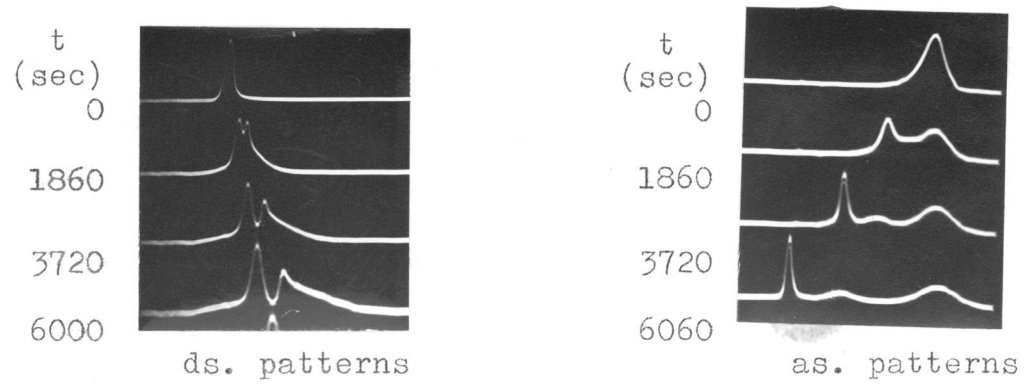
(B) M-1-1.

Component 1: PVA (1.03 g./100 cc.)
Component 2: S-2 (0.85 g./100 cc.)
E = 3.08 v./cm., μ_s = 0.111.

Fig. 15. Schlieren patterns of two component system.
Buffer: CH_3COOK-CH_3COOH, pH =6.2.
Sample: PVA (P = 1700), S-2 (P = 890, S = 2.50 mol.%), S-7 (P = 890, S = 5.82 mol.%)



(C) M-3-1.
Component 1: S-2 (0.50 g./100 cc.)
Component 2: S-7 (0.50 g./100 cc.)
E = 2.84 v./cm., μ_s = 0.011.



(D) M-4-1.
Component 1: S-2 (0.74 g./100 cc.)
Component 2: S-7 (0,74 g./100 cc.)
E = 2.84 v./cm., μ_s = 0.051.

Fig. 15. (Concluded)

peaks were observed. (In M-3-1 and M-4-1, the peaks corresponding to the slow components were extremely small in the ascending channel. This anomalies will be discussed later.)

The peaks of S-7 in M-3-1 and M-4-1 in the descending channel were remarkably unsymmetrical. The delta-boundary was explicitly observed in all cases except M-1-1 in which a higher ionic strength was chosen.

In Table 20, the mobility values are shown. For comparative purpose, the mobility obtained in one-component system was also illustrated. From this table, it is seen that the (descending) mobility in two-component system is of the same order of magnitude as that in one-component system. In multicomponent systems, because of changes of concentration and pH during electrolysis it is only for the fastest component in the descending channel that we can obtain the correct mobility. However, Table 20 indicates that it is possible to know reasonable, though approximate, mobilities of all of the constituents from the descending channel. This can be interpreted as indicating that, in our case, the passage of electric current does not give rise to remarkable changes in concentration and pH. It is dubious whether the same conclusion can be drawn in general cases or when the materials of higher charge density are contained.

(C) Mixing-Ratio of Components. When only the concentration of a component is altered at a boundary, the area of the pattern is expected to be proportional to the concentration. However, as Longsworth and MacInnes[80] supposed and Dole[77]

Table 20. Comparison of Mobilities in One and Two Component Systems

Buffer: CH_3COOK-CH_3COOH, pH = 6.2

(A) M-1-1.

Component 1: PVA (P = 1700)

Component 2: S-2 (P = 890, S = 2.50 mol%)

Mixing ratio (S-2/PVA) = 0.83, μ_s = 0.111.

	C_1	C_2	$m_1' \times 10^5$	$m_2' \times 10^5$	$m_1 \times 10^5$	$m_2 \times 10^5$	E
M-1-1	1.03	0.85	1.24	4.26	0.89	2.27	3.08
one comp.	0	0.82	-	4.91	-	2.97	3.03
	1.03	0	1.51	-	1.02	-	3.03

(B) M-4-1.

Component 1: S-2

Component 2: S-7 (P = 890, S = 5.82 mol.%)

Mixing ratio (S-7/S-2) = 0.95, μ_s = 0.05.

	C_1	C_2	$m_1' \times 10^5$	$m_2' \times 10^5$	$m_1 \times 10^5$	$m_2 \times 10^5$	$m_{del} \times 10^5$	E
M-4-1	0.78	0.74	8.36	10.27	2.47	6.21**	2.37	2.84
one comp.	0.82*	0	4.91	-	2.97	-	-	3.03
	0	0.67	-	9.78	-	7.96	-	0.35

* measured at μ_s = 0.1, ** calculated from the first moment.

C: component concentration in g./100 cc. indicated by the suffix.
m': ascending mobility, m: descending mobility.

has concluded, simultaneous change of the concentrations of all components actually takes place and the refractive fractions

of components deduced from the area of the pattern are divergent from the analytical ones. This deviation was studied and recorded in Table 21. According to this table, the ratio

Table 21. Fractions of Components Estimated from the Pattern

	comp. 1	comp. 2	C_1	C_2	C_2/C_1	$(S_2/S_1)_{obs}$ as.	$(S_2/S_1)_{obs}$ de.	$(S_2/S_1)_{cal}$	μ_s
M-1-1	PVA	S-2	1.03	0.85	0.82	0.48	0.89	0.54	0.111
M-1-2	PVA	S-2	0.43	0.35	0.82	0.46	0.79	0.72	0.111
M-3-1	S-2	S-7	0.50	0.50	1.00	*	0.93	1.26	0.011
M-4-1	S-2	S-7	0.78	0.74	0.95	**	1.39	1.00	0.051

* infinitely large. ** 1.85, not so accurate.
$(S_2/S_1)_{obs}$: observed ratio of pattern area. $(S_2/S_1)_{cal}$: see §4, (A).

of observed areas in the descending channel, $(S_2/S_1)_{obs}$ in the eighth column, is in good agreement with the analytical value given in the sixth column, whereas, in the ascending side, there is no agreement between them. This anomaly becomes striking in the case of M-3-1: the peak of a component is hardly detectable. We will not discuss the details here beyond making mention of the tendency that the anomaly is noticeable when the ionic strength is low and the materials of higher charge density are concerned.

(D) Displacement of Delta-Boundary. Since Tiselius found

out the delta-boundary[82] and Longsworth and MacInnes discovered the epsilon-boundary,[80] a wealth of research on the interpretation of these boundaries has been accumulated. These were firstly thought to be due to slowly migrating constituents but this possibility can be entirely eliminated according to our present study, because we are dealing with well-defined components. Dole's theory of moving boundary can answer the question why these boundaries appear. A mathematical conclusion of this theory requires the presence of a stationary boundary which remains at the initial boundary. This is the delta- or epsilon-boundary. However, if we consider that the fundamental assumption of this theory is of the nature which applies to only the dilute solutions of simple electrolyte, it is expected that the theory certainly fails in our solutions. In Table 22, the displacement of the delta-boundary is recorded in terms of mobility calculated from the moving velocity of the peak. The lack of data of epsilon-boundary is due to difficulty encountered in the observation. Under the experimental con-

Table 22. Displacement of Delta-Boundary

	μ_s	E	$m_{del} \times 10^5$
M-2-2	0.011	3.03	1.86
M-3-1	0.011	2.84	2.30
M-4-1	0.051	2.84	2.37

ditions in this table, the delta-boundary can migrate in an opposite direction to the moving boundary corresponding to the macro-ions. Care must be taken of the tendency that the displacement becomes smaller with decreasing potential gradient. Because the decrease of the gradient means a decrease in the total amount of electricity at a fixed specific conductance of the solution, the volume change of the electrode in the course of electrophoretic run appears worthy to be ascribed the above tendency. However, as mentioned already, the correction due to this change remains negligibly small. Therefore, other explanations have to be found.

Most recently, Hayashi and Oda[83] reported the similar finding in fibroin solutions. The voltage gradient was fairly high (about 10 v./cm.) in the buffer solutions of low ionic strength.

§ 4. Discussion

(A) Apparent Refractometric Fractions of Components. The deviation of the ratio of areas in the ascending pattern from the analytical mixing-ratio has been exposed in the foregoing section. This is thought to be due to the facts that (1) the specific refractive index increments are not in general the same for different components and (2) concentration difference of all the components exists across every moving boundary. These superimposed concentration differences will be analysed

here on the basis of the moving boundary equation, a statement of the conservation of mass.

An initially sharp boundary between two solutions, one of which contains a kind of polyelectrolyte in addition to the buffer ions, will split into a number of boundaries, on passage of an electric current. A schematic representation of such a system is given in Fig. 16. If the current is taken as flowing from left to right, for anionic polyelectrolyte the boundaries $\alpha\beta$, $\beta\gamma$, $\gamma\varsigma$ and $\varsigma\eta$ represent the ascending, delta, descending and epsilon boundaries, respectively. With these notations, we have two relations for the boundaries

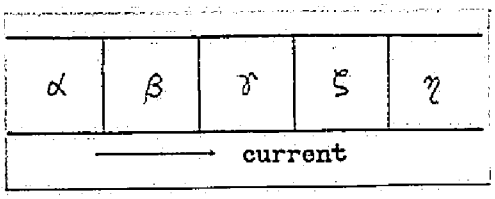


Fig. 16. Schematic representation of electrophoretic boundaries.

$$T_j^{\beta} - T_j^{\alpha} = V^{\beta\alpha}(C_j^{\beta} - C_j^{\alpha}), \qquad (6\text{-}1)$$

and

$$T_j^{\gamma} - T_j^{\beta} = V^{\gamma\beta}(C_j^{\gamma} - C_j^{\beta}), \qquad (6\text{-}2)$$

which are expressions of the law of conservation of mass, where T_j denotes the transference number of the j ion in the phase indicated by the superscript, V the boundary velocity per unit flux across it (taken as a positive value when the boundary travels towards the cathods), C_j the equivalent con-

centration of an ion of the species j (taken as negative for an anion and positive for a cation). In the α phase, macro-ions desappear so that we obtain

$$C_p^{\alpha} = 0 \text{ and } T_p^{\alpha} = 0, \quad \text{(p denotes the macro-ion.)}$$

and

$$T_p^{\beta} = V^{\beta\alpha} C_p^{\beta} . \tag{6-3}$$

Moreover, from (6-1) and (6-3) we obtain

$$T_p^{\alpha} = V^{\gamma\beta}(C_p^{\gamma} - C_p^{\beta}) + V^{\beta\alpha} C_p^{\beta} . \tag{6-4}$$

The similar consideration in the ascending side leads to

$$T_p^{\gamma} = V^{\gamma\varepsilon} C_p^{\gamma} . \tag{6-5}$$

From (6-4) and (6-5), the concentration of the macro-ions in the β phase, C_p^{β}, is given by

$$C_p^{\beta} = C_p^{\gamma} (V^{\gamma\varepsilon} - V^{\gamma\beta})/(V^{\beta\alpha} - V^{\gamma\beta}). \tag{6-6}$$

Actually we know that $V^{\beta\alpha} \gg V^{\gamma\varepsilon}$ when the ionic strength is low, so that C_p^{β} would be smaller than the original concentration, C_p^{γ}. On the other hand, the moving boundary equation, for example (6-1) or (6-2), requires that $\bar{V}$ is dependent on the concentration dependence of the transference number. Since this dependence would vary with the charge density of polyelectrolytes which are concerned, $C_p^{\beta} / C_p^{\gamma}$ would be not the same for different polyelectrolytes.

If the transference number of the macro-ion would not be

affected by the presence of another kind of macro-ion, the phases developed on passage of an electric current in the multicomponent system can be interpreted as a superposition of those which will be separated in one-component system. If this is a permissible approximation, the apparent refractometric fractions of components should be compared with the ratio of C_p^β's given by (6-6), not with the original analytical fractions, when small concentration differences of the buffer ions can be assumed to be negligible. Comparison of this kind was undertaken in Table 21, in which the ratio of C_p^β's given by (6-6) was denoted by $(S_2/S_1)_{cal}$. This value is always in rough agreement with the fraction of a component obtained from the area of the pattern, refractometric fraction.

There is a trend in the difference between $(S_2/S_1)_{cal}$ and C_2/C_1. This difference is large when a higher polymer concentration is chosen at a fixed ionic strength (compare M-1-1 and M-1-2), and when a lower ionic strength is chosen at a fixed polymer concentration (compare M-3-1 and M-4-1). The assumption of the boundary superposition mentioned above presupposes absence of interactions between different kinds of polyelectrolytes. This presupposition will be invalid when the polymer concentration becomes great and the ionic strength is low. The observed trend shows validity of the presupposition and importance of the inter-macro-ion interaction stressed in Chapt. 2. (In the comparison, V in (6-6) was evaluated

from the displacement of the peak of the pattern. Because of the unsymmetry of the pattern, it should be calculated using the first moment. If this value is used for S-7 in M-3-1 and M-4-1, the somewhat small $(S_2/S_1)_{cal}$ is obtained.)

(B) Displacement of Delta-Boundary. It was shown that the delta-boundary can travel under certain conditions. As stated above, the Dole theory asserts that one of newly developed boundaries on passing of an electric current must be stationary, but the assumption, that the relative mobilities (relative to the mobility of a species of ion taken as unity) are constant, can not represent a close approximation when the interionic interaction is remarkable. The satisfactory agreement between the theory and experiment was reported by Longsworth for aqueous solutions of strong electrolytes.[84] However, as will be expected from the assumption, the theory would be invalid for the polyelectrolyte solutions, which have the numerous charges on a molecule. The failure will be most concisely demonstrated in the disagreement between the number of charges of a macro-ion determined by titration and that calculated by the application of the Dole theory. Accordingly our finding of the moving of the delta-boundary is not unexpected.

A question how to introduce a correction term due to the deviation of our system from the ideality treated by Dole into his original theory has to be answered. General and prac-

tically useful extension of the Dole theory can not be easily obtained because of mathematical complexiety. Our following discussion on this problem will be limited to a semi-quantitative aspect, also. For the sake of simplicity, one-component system is treated. Consider that, on application of an electrical potential, the boundary system will develop as shown in Fig. 16. The assumption, that the relative mobilities are constant, requires that the difference between the transference numbers of two phases is dependent only on the concentration. Therefore, if the delta-boundary is stationary ($V = 0$), the moving boundary equation, (6-2), reduces to

$$T_j^{\beta} = T_j^{\gamma}.$$

Then, all species of ions are to be diluted by a dilution factor at this boundary. From this consideration, the experimental fact of $V \neq 0$ is seen to be ascribed to imperfection of the fundamental assumption of the theory. According to the moving boundary equation, for $V^{\beta\gamma} > 0$,

$$|C_j^{\beta}| > |C_j^{\gamma}| \quad \text{and} \quad T_j^{\beta} < T_j^{\gamma} \tag{6-7a}$$

or

$$|C_j^{\beta}| < |C_j^{\gamma}| \quad \text{and} \quad T_j^{\beta} > T_j^{\gamma} \tag{6-7b}$$

must be satisfied. As Longsworth and MacInnes shows,[80] since in the usual case $|C_j^{\beta}| < |C_j^{\gamma}|$, our experimental results conform with (6-7b). Furthermore, (6-7b) and the definition of transference number give

$$m_j^{\beta} C_j^{\beta}/\varkappa^{\beta} = m_j^{\gamma} C_j^{\gamma}/\varkappa^{\gamma} \quad , \tag{6-8}$$

where $\varkappa$ denotes the relative conductance. If we assume $\varkappa^{\beta} = \varkappa^{\gamma}$ provisionally, (6-8) gives

$$m_j^{\beta} C_j^{\beta} > m_j^{\gamma} C_j^{\gamma} \quad , \tag{6-9}$$

which means that the mobility m decreases with increasing concentration C. Our experimental results for S-7 described in Chapt. 5 indicate that the mobility of macro-ions went down with the concentration in a range of 0 - 0.8 g./100cc., when ionic strength was 0.05. (The observed mobility is not the relative one, but the concentration dependence of the mobility is so striking that the mobility of small ions can be regarded as independent of the concentration and the observed mobility can be used in the place of the relative one so far as the concentration dependence of a property is discussed.) For lower ionic strength, also, the same tendency will be observed. Thus experimentally $V \neq 0$ must be observed. Actually, moreover, we should expect that $\varkappa^{\beta}$ is smaller than $\varkappa^{\gamma}$ because the concentrations of ions present in the β phase are lowered. If it is true, and when the difference between the relative conductances is not so large, the displacement of the delta-boundary towards the cathod will be found even when the mobility has not so a marked concentration dependence as required by (6-9).

As would be understood from the above considerations, the displacement of the delta-boundary towards the cathod is determined by the tendency of decreasing of the mobility of the macro-ion with its concentration. This dependence was interpreted in terms of the interionic interaction as mentioned in Chapt. 5. A large volume effect is responsible for a minimum and rise in the concentration dependence of the mobility. The minimum will shift towards smaller concentrations as the volume effects become noticeable. Hence only the monotonical increase will be observed when the volume effect is extremely striking. Then, on the contrary to our observation, the delta-boundary will travel towards the anode. At any rate the moving of this boundary can be ascribed to the interionic interaction.

(A conclusion obtained by Svensson[78] and Longsworth,[79] that the delta-boundary can be eliminated in the cases of low polymer concentrations and high ionic strengths, can be interpreted in terms of this interaction. It is interesting to see that the interaction is diminished in these cases. In other words, the appearance of the stationary boundary can be attributed to the interaction. Therefore it might be wrong to assert that the Dole theory, which explains the existence of the stationary boundaries, is dealing with an ideal state only.)

In the above discussion, the considerations were limited to one-component system. Needless to say, they are applicable to multicomponent systems in principle. It must be noted that,

in this application, a simple algebraic sum of concentrations of all components can not approximate the actual concentration effect.

Finally mention should be made on the effect of potential gradient on the displacement of the delta-boundary. Dole's theory can never give answer to this problem. We consider that change of the concentration dependence of mobilities with the gradient is responsible for this effect. Wall's experiments[48] show that the fraction of counter-ions which travels with macro-ions in an electric field decreases with increasing potential gradient within the range of 0.15 - 1.4 v./cm. If this result can be applied to our case, the effective number of charges of a macro-ion (analytical number of charges minus number of counter-ions fixed by a macro-ion) must become larger with growing potential gradient. The more greater the effective number of charges becomes, the more sensitively the mobility varies with the concentration. Accordingly deviation from an assumption of constant relative mobility would become greater and the delta-boundary begins to migrate.

Note. Most recently, the problem analogous to what we treated in this chapter was analysed by Nichol and Gosting[85] A similar way of approach to weak electrolyte moving boundary system as Dole's was reported by Nichol et al.[90]

CHAPTER 7

AN APPROACH TO ADSORPTIVE SMALL ION BINDINGS OF POLY(VINYL ALCOHOL)

Sakurada and Inoue[87] pointed out the existence of carboxyl groups in poly(vinyl alcohol) (PVA) molecules about a decade ago. Recently Sakurada and Yoshizaki[67] reported the quantitative determination of the groups by means of conductometry and asserted, on the basis of the mechanism of the polymerization of vinylacetate, that the carboxyl groups existed as an end group of a PVA molecule. Hosono and Sakurada[68, 73] tried to treat the problem from an electrophoretic point of view. If the PVA molecules contain the ionizable groups such as carboxyl groups, the molecule is to migrate towards the anode. This was really the case.

However, detailed quantitative analysis of the electrophoretic mobility of PVA was followed by a difficulty in interpreting the unexpectedly rapid movement (hence, the great number of charges). The Debye-Henry relation, (5-2), when combined with the observed mobility, gave much larger number of charges than that expected from conductometry. The discrepancy was attributed to adsorption of small ions by PVA molecules and analysed by a method proposed for proteins by Klotz and Curme.[88] The number of charges estimated from the mobility (excluding that due to the ionizable groups) was shown to be

in a binding equilibrium and the striking salt concentration dependence of the mobility of PVA was successfully explained. The number of binding points was determined to be about six per 100 basic molecules of PVA. Such an analysis, in spite of its success in establishing the quantitative relation, leaves a question regarding the mechanism of the binding, which we intend to put under investigation in this chapter.

Evidence of the interactions between polyelectrolytes (both synthetic and natural) and small ions was reported very abundantly. It must be mentioned that there are two types of interactions: firstly a case, that the macromolecules form a complex compound with these small ions, is of importance in considering the behaviours of proteins in salt-containing solutions, and secondly another case, to that we consider electrostatic effects can give a satisfactory interpretation, is usually observed for polyelectrolytes. In the first case which differs from the second in the conditions imposed by the coordination number and the steric requirement of the complexing ion, it is important to realize, that highly specific interactions between the macromolecule and small ions may be superimposed on electrostatic effects. It may be useful to make mention of these two categories here.

The polyelectrolyte carries a high net charge so that the attraction between the macro-ion and its counter-ions is sup-

posed to be very predominant. The electrostatic potential energy near the macro-ion is not small compared to the kinetic energy. Therefore a fraction of the counter-ions present within a region in close proximity to the macro-ion appears to lose their freedom to get free out of the influence of the macro-ion. This fraction can not be independent kinetic entities: this effect may be responsible partly for usually small ionic activities and osmotic pressures. It was this kind of interaction that Wall et al.[17] called "counter-ion fixation". The examples are found in the system composed of poly(acrylic acid) and sodium or potassium ions as the counter-ion. Although any convincing theoretical argument appears to be still lacking to us, the treatment would be comparatively simple because no other than Coulombic forces intervenes.

On the other hand, another kind of interaction (first case) will occur even for unionized macromolecules and polyampholytes at the isoelectric point. Specific groups participate in complex formation. Accordingly, other than Coulombic forces must be involved. The examples are the poly(acrylic acid) or poly(methacrylic acid) - cupric ion system, which was investigated by Wall, Gregor, Kotliar et al.[89] They inferred that chelate formation must be involved with two carboxylate groups. Another interesting example is quaternized poly(vinyl pyridine) which may acquire a negative charge in solutions of high bromide concentration.[90] Since this polymer is positive-

ly charged in solutions of low bromide concentration, the phenomenon proves that the ionized groups can bind more than an equivalent amount of counter-ions and any other force, in addition to electrostatic one, needs to be taken into account in order to obtain the comprehensive explanation.

Let us come back to our present problem. To which of the above mentioned two types of interactions does the adsorptive binding by PVA molecules belong? Answering to this question is very simple if we notice that the PVA molecule can bind the negatively charged ions against the repulsive force between these ions and ionized groups. It is clear that an attractive force is working much more predominantly than the electrostatic repulsive force. And it is not extravagant to assume the attractive force between the PVA molecule and the small ions to be due to the ion-dipole interaction. In the following considerations, we will try to obtain a quantitative description of the existing experimental data as an extension of Langmuir's isotherm. The possibility of complex formation is beyond the scope of our discussion.

Dipole Moment of a PVA Molecule. The dipole moment of a PVA molecule was not determined experimentally because non-polar solvents could not be found out. Approximation must be carried out.

Sakurada and Lee[91] have made studies on the dielectric

properties of a number of neutral polymers. They demonstrated that the electric moment of the corresponding monomeric molecule was in good agreement with that of the basic molecule. For example, the dipole moment of basic molecule of poly(vinyl acetate) agrees with that of vinyl acetate. This result was interpreted as signifying that the polymer chains, so far as the dielectric properties are concerned, were so flexible. It appears to us reasonable to apply this observation to PVA, which can be supposed to have nearly the same degree of flexibility as poly(vinyl acetate). We can thus assign the value of the dipole moment of ethy alcohol (1.7 in Debye unit) to the partial dipole (basic molecule) of PVA. This approximation is naturally open to criticism, especially in the case of aqueous solution. The orientation effect of water molecules, which would possibly occur actually, raises great difficulties in treating the present problem. Such an effect, however, should be taken into account when our approximation yields fatal error.

For the sake of simplicity, the interaction between this partial dipole and the salt-ions and that between the salt-ions are taken into consideration. The dipole obviously attracts a certain amount of positive ions into a region near the negative pole and at the same time the same quantity of negative ions near the positive pole. If this is really the case, however, the dipole could not migrate in an electric

field. The experiment gives the negative mobility for PVA and shohld be interpreted as signifying that the negative ions can be adsorbed predominantly. This selectivity can not be reflected unless the negative pole is assumed to be inaccessible to the positive ions. This assumption is admittable when we consider bond moment of ethyl alcohol, of which the total dipole moment can be resultant to a first approximation. The bond moment of bonds in consideration is shown in the following table, in which the positive pole is in the first column and the moment is expressed in Debye unit.

Table 23. Bond Moment of Ethyl Alcohol

+	-	bond moment
H	C	0.3
C	O	0.9
H	O	1.5

From these data, we can conclude that the outer part of the molecule is positively charged, and only the negative ions can approach to the PVA molecule.

Number of Adsorbed Ions. In order to estimate the number of adsorbed ions on the PVA molecule, we will use assumptions of adsorption equilibrium made by Langmuir,[92] which was derived from assumptions that the adsorbed molecules exist in monolayer on the solid surface and the velocity of adsorption can be equalized to that of desorption at equilibrium. Though it forms a good basis for the discussion of the adsorption of gases on so-

lids, the applicability is strictly limited to an idealized solid surface, chemically inert and impermeable to the adsorbed (ideal) gases, since negligible interaction between the adsorbed molecules in addition to the above assumptions, was also assumed. It must be mentioned furthermore that there was no specification of the nature of adsorption force. In this respect, Fowler and Guggenheim[12] have shown that a parameter, b, originally given by Langmuir as a ratio of velocity constants of adsorption and desorption, in the isotherm

$$X = A/(1 + b^{-1}C^{-1}) \ , \qquad (7\text{-}1)$$

where X is the number of adsorbed molecules, A the number of adsorbed molecules in saturation, C the concentration of gas-molecule, is expressed by

$$b = \exp\left\{(u_o - u_a)/kT\right\} \ , \qquad (7\text{-}2)$$

where $u_o - u_a$ denotes the heat of adsorption per molecule. Such a statistical consideration allows us to find a clue to apply (7-1) to our problem. It is clear that (if a partial dipole, basic molecule of PVA, is assumed to be a site capable of adsorbing an ion) the potential energy due to the interactions between the adsorbed ion and dipole and between the adsorbed ions and free ions should be introduced in the place of the heat of adsorption.

The potential due to a dipole (moment strength = μ) is given as a function of distance r from the centre of the di-

pole by

$$(\mu/\epsilon r^2)\cos\theta \ , \qquad (7\text{-}3)$$

where θ denotes an angle between the dipole vector and the line connecting the centre of the dipole and a point considered, and ϵ the dielectric constant of the solvent. In the present consideration, the case of $\theta \neq 0$ will be excluded because the maximum stability is obtained at $\theta = 0$. The problem, then, reduces to one-dimensional.

The potential of the dipole-ion interaction is of short range. Therefore the interaction will decrease so steeply with increasing r from the surface of the basic molecule that the adsorbed ions can be assumed to be in the monolayer. Then the interaction between the partial dipole and the ions in contact with the former is given by

$$\mu/\epsilon\delta_1^2 \ , \qquad (7\text{-}4)$$

where δ_1 denotes the distance between the centres of the dipole and the adsorbed ion.

The repulsive interaction potential between the adsorbed ion and the free ion, in the current electrokinetics, is treated as an unknown factor, that is determined experimentally. However, since the determination can not be carried out in our case, the electrostatic potential at the monolayer is a priori assumed to be $-e_o/\epsilon\delta_2$, where δ_2 denotes the radius of ion assumed to be a rigid sphere. If we further assume that the

distribution of ions is determined by the Boltzmann formula, the number of adsorbed ions (negative and monovalent), x^-, will be given by

$$x^- = A/\left[1 + C^{-1}\exp\left(\frac{e_o\,\mu}{\epsilon kT\,\delta_1^2} - \frac{e_o^2}{\epsilon kT\,\delta_2}\right)\right]. \qquad (7\text{-}5)$$

Implications of (7-5) will become clear if we compare this relation with (7-1) and (7-2). The energy required to evaporate an adsorbed (negative) ion in the electric potential field is naturally less than that in the absence of the field.

The assumption that the electrostatic potential at the monolayer is $-e_o/\epsilon\delta_2$ may be seriously objected. We assumed above one-to-one correspondence of a partial dipole and an ion: in other words, a partial dipole represents an adsorption site. Even at saturation, however, the site can not be occupied by an ion. Therefore the above assumption clearly overestimates the potential since $-e_o/\epsilon\delta_2$ also represents the potential of a negatively charged rigid sphere. This would lead to an overestimation of A, when (7-5) is combined with experimental results. (This statement applies to a single dipole, when it exists independently from other dipoles. In actual case, the dipoles considered here are bound together on a polymer chain. Consequently, the adsorbed ion on a dipole exerts a repulsive influence on ions of the same sign present in the neighbourhood of other dipoles. Such an effect is completely

neglected in our consideration. However this neglection might unexpectedly cancel out the overestimation mentioned above and hence reasonable agreement with experiment might happen to be obtained.)

(7-5) was tested with Hosono and Sakurada's data. The numerical values used were $\delta_1 = 2$ A., $\delta_2 = 1$ A., $\mu = 1.7$ Debye and $\epsilon = 80$. The result of this test is in Table 24, in which A is calculated using observed x^-. According to the application of the Klotz extrapolation method, the maximum number of adsorbed ions was 0.6×10^{-1} which is not so far from A's found here. The disagreement is related to an overestimation of the potential of monolayer but it is not so serious.

Table 24. Calculated Number of Adsorbed Ions in Saturation

μ_s	$x^- \times 10^3$	A x 10
0.1	6	1.06
0.01	0.6	1.05

The dipole moment of the basic molecule was assumed to be 1.7 Debye. This quantity can never be ascertained experimentally. However because of the predominancy of Coulombic potential, we will have nearly the same A-value, even if we adopt other values for the dipole strength than 1.7.

It seems desirable to make mention of an analogy between the situations encountered in choice of the free energy of polye-

lectrolyte solutions and in interpretation of the dipole strength of the basic molecule which is independent of the degree of polymerization. Sakurada and Lee[91] have shown that this dielectric property can be explained if we admit that end-to-end distance of the polymer chain is proportional to the square root of degree of polymerization. This means, as pointed out by them, that the partial dipoles can behave independently from each others except that they can not diffuse away into the bulk of the solutions. The indiffusibility would give rise to a difference between the dipole moment of basic molecule and that of the corresponding monomeric compound, just as the character of macromolecules referred to in Chapt. 2 resulted a finite difference between the free energy values of simple and polymeric electrolytes. However, it is too small due to weakness of the dipole-ion interaction to be regarded as practically serious.

Care must be taken, however, of the dielectric constant, which has a great effect on the result. Collie et al.[93] reported that it decreases with decreasing interionic distance (r'), say to 4.7 for r' = 1 A. But, at present, their calculation can not yet be checked experimentally and so we can not help admitting use of the macroscopic value. It may be useful to note that smaller A would be resulted when smaller ϵ is used.

In view of Stern's theory[94] on the zeta-potential against

electrolyte concentration relation, we should notice that its specific adsorption potential was specified as the dipole-ion interaction potential in our treatment. This approach has to be put under further investigation in the light of information which was or will be obtained by other experimental methods using a variety of polar polymers. Electrophoretic movement of poly(phenylene) in pyridine-water mixtures (pH = 8.8) was reported, which is expected to be interpreted in terms of the same interaction between chlor atom at the end of the molecule and pyridinium ion, as was treated here. The charge reversal of cationic poly-4-vinylpyridine derivatives in potassium bromide solutions[90] was attributed to the binding of bromide ions in excess of the stoichiometric equivalent. The excess binding may also be due to the dipole-ion interaction since the Coulombic interaction is now suppressed. The dipole moment of pyridine is somewhat higher than that of ethyl alcohol and the effect of this interaction might be more easily observed. At any rate, this interaction appears, so far, to give a fairly satisfactory interpretation of the behaviour of PVA in salt-containing solutions.

CHAPTER 8

GENERAL DISCUSSIONS

In the foregoing, thermodynamic properties of polyelectrolyte solutions have been discussed. A standpoint was checked that the macro-ions can conduce to formation of an ionic atmosphere. This, however, is not novel, but has been already suggested by Debye and Hückel for simple electrolyte solutions, and succeeded to Wicke and Eigen. Because of the pronounced volume effect of the macro-ions, this standpoint has not easily been taken for granted in the previously published theoretical approach in this field. However the fact that our consideration could give a unified interpretation of some phenomena appears to be a good basis for asserting correctness of our standpoint. Of course, there are still a great number of problems to be studied in future. An irreversible process of these solutions was hardly treated and examined in this record, which we believe can be at least qualitatively interpreted from the standpoint. In our approximations themselves, there are left some points to be reexamined. For example, the assumption of the same dielectric constant of the medium inside and outside the macro-ion naturally has to be removed when the extension of our treatment is intended to the typical polyelectrolytes of a larger number of charges.

In numerous attempts to extend the Debye-Hückel theory from the dilute solutions of simple electrolytes to higher

concentrations, included are the electrostatic interaction theory such as Wicke and Eigen's, from which our present interpretation was developed, and the ion-solvent interaction theory such as Stokes and Robinson's.[9] The basic idea in the former category that the ions can form an ionic atmosphere has gained public recognition, and has not essentially been altered in the Wicke-Eigen theory. It is interesting to notice that, in the former category, the electrolyte solutions were treated ultimately as an ionic gas: though the dielectric constant of the solvent was introduced, the continuity of the solvent was also assumed. (This assumption must be removed when the higher concentrations are dealt with.) Such a simplification makes us pay attention to an analogy between electrolyte solutions and plasmas which are consisted of completely ionized atoms in the low density and high temperature. Really the thermodynamic quantities of the plasmas were derived by Cowan and Kirkwood[95] on the ground of the Debye-Hückel theory. Because of unsolved difficulties in generating the plasmas, experimental examination is not yet reported. (In this respect, we must mention solubility measurements of a simple electrolyte by Lietzke[96], which showed the validity of the Debye-Hückel theory at 200°C.) When such an approach will be further continued, we could find out the new development in interpreting properties of the electrolyte solutions and the plasmas, from which useful suggestion will also be obtained for treatments

of our problem.

The ion-solvent interaction theory is concerning with the hydration of the ions, and can also successfully describe the experimental data of activity coefficient up to 5 mole/l. for NaCl. It is interesting that the two categories originate from the recognition of a phenomenon, hydration of the ions, which would give rise to the exclusion effect of the ion according to Wicke and Eigen's terminology. This effect, in addition to the assumption of penetrability of the oppositely charged ions, was a clue to our present consideration. Therefore we might expect the more fruitful results by application of the ion-solvent interaction theory to our problem, than those obtained by means of Wicke and Eigen's distribution formula, though that theory contains two adjustable parameters, the number of water molecules hydrated by the ions and the closest distance approach.

Apart from the problems just mentioned to belong to the research in future, we must make mention of the points of general interest at present. First of all, the problem of counter-ion fixation is important. Advancement in the experimental aspect has not been accompanied by exploration of a theoretical nature. Our assumption in this record, that the number of counter-ions "associated", according to Wall's terminology, could be taken as λ , may be challenged at least because the mechanism of the association seems to remain un-

solved. Recently Wall[97] proposed a treatment and Harris and Rice's work[21] also represents an interesting attempt to treat the problem quantitatively. However we believe that these treatments overestimate the number of associated counter-ions. In short, a boundary condition adopted in Wall's work, $d\phi/dx = 0$ at $x = X$, where $\phi = z e_o \psi/kT$, $x^2 = 4\pi n' z^2 e_o^2 r^2/\epsilon kT$, $X = (x)_{r=R'}$, R' denotes the radius of the larger sphere which is taken to be the average volume of the solution associated with each polymer molecule, n' the average number of counter-ions per unit volume, seems to underestimate the interaction between small ions and all ions present in the system besides the central macro-ion. As for H-R's treatment, we should like to point out that the W-E distribution formula should be preferred to the Boltzmann distribution for small ion existing inside the polymer sphere as the neglection of the volume effect would lead to an overestimation of the number of associated small ions. We believe that the essential feature is still the electrostatic effect of other (macro-) ions. In Bjerrum's theory mentioned in Chapt. 1, such an effect could be safely neglected because of the short distance between associated and central ions and because of the low valency of the ions. Thus the average number of ions of the opposite charge within the sphere $r = q$, a characteristic length mentioned in Chapt. 1, round the central ion could be expressed by

$$n\int_{a}^{q} \exp\left(ze_0^2/\epsilon kT\, r\right) 4\pi r^2\, dr, \qquad (8\text{-}1)$$

where n is the number concentration of the oppositely charged ion per unit volume of the solution, a the closest distance of approach and others are defined in Chapt. 2. This treatment successfully described the experimental results, especially of bi-bivalent simple electrolytes, and of the uni-univalent electrolytes in solvents of lower dielectric constant. However the direct application to our cases resulted in a considerably smaller number of associated ions than that found out experimentally. In view of this discrepancy, that the electrostatic potential due to other macro-ions is not zero at a position of the central ion appears to be the cause. If this reflects the reality, the potential used in (8-1) can be said to be too small and hence the attraction force, to which the counter-ion association is to be ascribed, is unrealistically underestimated. This means that the inter-macro-ion interaction plays so important role in the polyelectrolyte solutions that it can not be ignored. Though a quantitative representation of the revised calculation is omitted here, we should like to point out that the cause of failure of Bjerrum's treatment was the same as that mentioned in Chapt. 2 with regard to deficiencies of the previouly published theories of polyelectrolyte solutions.

Most recently, Strauss[98] tested the applicability of the

theories involving a polyelectrolyte model in which the macro-ion charge was smeared out over a sphere. He compared the observed zeta-potential determined electrophoretically with use of the Einstein theory of viscosity with the theoretically predicted potential and made mention of the great discrepancies. A theory, on which this interesting comparison was mainly based, was that proposed by Lifson.[19-B] From the result that the theoretical values are all considerably smaller than the experimental values, Strauss concluded that the polymer molecule was a chain which was loosely coiled even in solutions of simple electrolyte and that the potential of a cylindrical double layer which surrounded the chain was measured as the zeta-potential in electrophoresis. This discrepancy, however, can be interpreted as follows, in the light of our consideration: because of the neglection of inter-macro-ion interaction, the potential calculated by Lifson ultimately underestimates the reality. It is to be noted that this neglection was a cause of the failure of Bjerrum's method in the polyelectrolyte solutions. We can not agree with Strauss' conclusion that the smearing out of the macro-ion charge gives an over-simplified, unrealistic picture.

Secondly a comment must be given on the insensitivities of some properties of polyelectrolyte solutions towards the degree of polymerization, P. In these, included are electrochemical properties such as the fraction of associated counter-

ions[17], the equivalent conductance,[99] the electrophoretic mobility (see Chapt. 5) and the titration curve (see Chapt. 2). As mentioned in Chapt. 3, the titration behaviour is independent of the degree of polymerization because of cancellation of the charge effect and the extension effect. This is clearly the case with the electrophoretic mobility and possibly with the conductivity also. Strauss et al.[100] insisted that the insensitivity of the mobility is a further evidence for free drainage of the polymer coil. This interpretation contradicts their viscosity and light scattering results which indicate that the polyelectrolyte behaves as impermeable coils in solutions of simple electrolyte. Of course there might be a possibility that the theoretical requirement for impermeability as observed by viscosity measurements is not incompatible with that for free drainage as observed by electrophoresis. However, we take a standpoint mentioned just now because it can successfully apply to more than one case. As for counter-ion association, we are not in a position to give a convincing explanation for the insensitivity since the quantitative description of the problem is not yet well-established. However this property may serve as a basis for judging validity of the description when it will be proposed in future.

It is interesting that this insensitivity does not apply for extremely low P's. This was ascertained by Eisenberg on titration behaviour[101] and conductivity.[99] Recently an in-

crease of the conductivity with irradiation of gamma-ray was observed of sodium carboxymethylcellulose,[102] which was attributed to degradation by the irradiation. Since the degradation would result in a decrease in the number of charges per molecule, the attracting force between the macro-ion and the counter-ions would be weakened: an increase in the number of unassociated counter-ions is to be expected, which are capable of conducting an electric current. Thus, though this experiment and its interpretation contain some ambiguities, they appear to suggest something on the sensitivity of counter-ion association towards low P's.

We stressed the effect of interionic interaction on thermodynamic properties of dilute solutions of polyelectrolytes through the present record. The omission of this interaction was shown to lead us to failure in explaining the experimental results. The importance was firstly suggested by the success of Debye-Hückel's theory and Wicke-Eigen's theory. From an experimental point of view, Rosen, Kamath and Eirich[103] were the first to notice the unrealistic neglect of this interaction. We may be right to assert that the neglect is definitely incorrect. However, we wish to conclude by stating that the contribution of our present work, if any, would be its ability to pave the way for further advancement in this field and it is not yet the end of the story.

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SYNOPSES

Chapter 1. Theoretical interpretations of simple electrolyte solutions, which were proposed after the Debye-Hückel theory appeared, were summarised. The considerations were limited to the theories of a Debye-Hückel type and possibility of extending these theories to the polyelectrolyte solutions was discussed. The application of Wicke and Eigen's theory which takes notice of the volume effect of ions and of the penetrability of ions was suggested to be most promising. Attention was called to closeness of simple and polymeric electrolyte solutions.

Chapter 2. The basic idea underlaying the Wicke-Eigen theory of simple electrolyte solutions was examined. The distribution formula was applied to polymeric electrolyte solutions and thermodynamic quantities were derived. This means that inter-ionic interaction in the dilute solutions has been disposed. The activity coefficient and osmotic coefficient were found to have a tendency to decrease with polymer concentration and to increase through a minimum. A formulation of the "activity coefficient of macro-ion" has been obtained and was known to give a reasonable expression for the rate of change of the activity coefficient with the polymer concentration. The heat of dilution was also shown to be positive, on the contrary to the simple electrolyte solutions. (J. Polymer Sci., in press.)

Chapter 3. The treatment presented in Chapt. 2 was extended to the titration behaviours, which were obtained for poly(vinyl alcohol) partially acetalized with glyoxylic acid. The titration curve, arranged by a relation proposed on the assumption that the self-dissociation could not be neglected, showed that this polyacid was a fairly strong acid (pK_a^n = ca. 3). Information regarding the extension of the macro-ion was obtained from the electrostatic free energy change. The extension was found to have a tendency of decreasing sharply with polymer concentration, in conformity with the viscosity-concentration curve. The salt concentration dependence and the temperature dependence of the extension were known to be in good agreement with viscometric data. This success can be interpreted as signifying that the treatment can be a sound basis for discussing the nature of dilute solutions of polyelectrolytes. (Mem. Fac. Eng. Kyoto Univ., 19 402 (1957), Chem. High Polymers, Japan, 15 175 (1958), J. Polymer Sci., in press.)

Chapter 4. The viscosity measurements were performed with poly(vinyl alcohol) partially acetalized with glyoxylic acid, in solutions of simple electrolytes, to which Pals and Hermans' method of dilution was applied. It was found that the extension of a macro-ion on the dilution line was kept constant over a polymer concentration range, utilizing the treatment presented in Chapt. 3. A parameter, m, in the method of dilution was found not to be far from the ratio of activity coefficients of

polymeric and simple electrolytes. From these considerations, the "effective ionic strength" proposed by Pals and Hermans was suggested to be a significant quantity in dilute solutions of polyelectrolytes. (To be submitted to Chem. High Polymers, Japan.)

Chapter 5. Electrophoretic behaviours were studied of poly-(vinyl alcohol) partially acetalized with glyoxylic acid. The mobility was found to be almost independent of the degree of polymerization and to increase with the carboxyl group content. The mobility decreased steadily with the polymer concentration for materials of low charge density, while it went through a minimum for those of higher charge density. The mobility, moreover, decreased in the sequence of increasing ionic strength. Comparing the number of charges of this polyacid in buffer solutions by means of Debye-Henry's theory from the mobility and the value conductometrically determined, the applicability of the theory was confirmed to quantitatively describe the electrophoretic movement. (Mem. Fac. Eng. Kyoto Univ., 19 417 (1957), Chem. High Polymers, Japan, 15 339 (1958))

Chapter 6. The system containing two kinds of polyelectrolytes was electrophoretically studied. It was found that in the descending channel the ratio of areas of the patterns agreed with the analytical mixing ratio of the components whereas in the ascending one this was not the case. The discrepancy

was also found to decrease somewhat with taking the concentration dependence of the transference number of the polyelectrolyte component into account with the aid of Dole's theory, but the satisfactory agreement with the analytical ratio was not obtained. Moreover the distinct displacement of delta-boundary was observed in the opposite direction to that of the polymer component. This observation, together with the above mentioned disagreement, was suggested to be due to the interaction of electrostatic nature, which was discussed in Chapt. 2. (Chem. High Polymers, Japan, in press.)

Chapter 7. An approach was proposed on the basis of the dipole-ion interaction and Langmuir's theory of adsorption, to the adsorptive binding of poly(vinyl alcohol) which was found electrophoretically. Assuming that the partial dipole is capable of binding a small ion and its strength is equal to that of ethyl alcohol, the attracting force between the dipole and the ion and the repulsive force between the adsorbed and free ions were introduced into Langmuir's isotherm. The analysis of experimental data by means of this treatment gave the number of adsorbed ions in saturation, which agreed with the value obtained from the electrophoretic mobility by Klotz's method. (Unpublished work)

Chapter 8. Importance of the basic idea that the macro-ions can form an ionic atmosphere was again stressed. Possibility of application of the ion-solvent interaction theory was sug-

gested. Recent theories which dealt with the counter-ion association, a characteristic phenomenon of polyelectrolytes, were critically examined. An argument proposed most recently by Strauss was criticized from the idea just mentioned. The insensitivity of electrochemical properties of the solutions towards the degree of polymerization was mentioned.

APPENDIX: LIST OF SYMBOLS

The following is a compilation of the notations which were frequently used in the present record.

A = number of adsorbed ions in saturation.

a = closest distance of approach.

B = second virial coefficient.

C_p' = concentration of polyelectrolyte (g./100 cc.).

C_p = concentration of polyelectrolyte.

E = voltage gradient (volt cm^{-1}).

e_i = charge of ion indicated.

e_o = elementary charge taken as the absolute value.

F_e = electrostatic free energy.

g = osmotic coefficient.

k = Boltzmann's constant.

k' = Huggins' constant.

K_o = dissociation constant of ionized groups in an ideal state. ($pK_o = -\log_{10} K_o$)

L_p, L_s = total number of macro-ions or salt-ions.

m = mobility, or Pals-Hermans' parameter.

m_p^-, m_p^+ = exclusion volume parameter of negative macro-ion and positive gegen-ion.

m_s = exclusion volume parameter of negative and positive salt-ions.

m_2 = concentration of polyelectrolyte in mol./l.

m_3 = concentration of added salt in mol./l.

n_p, n_s = average number concentrations of macro-ions and salt-ions.

$p^{n^-}r$, $p^{n^+}r$, $s^{n^-}r$, $s^{n^+}r$ = average local concentration of ion indicated at a distance r from a central ion.

N_p^-, N_p^+, N_s = number of sites which ions indicated can occupy in unit volume of the solution.

P = degree of polymerization.

Q = number of charges of a macro-ion.

R = radius of spherical macro-ion,

R_e = radius of spherical macro-ion estimated with Einstein's theory of viscosity.

S = carboxyl group content (mol. %), or area of Schlieren pattern.

T = absolute temperature, or transference number.

X = concentration of foreign salt.

X_o = effective ionic strength.

x_- = number of adsorbed negative ions on PVA.

v = exclusion volume of ion, for example, $v_p^- = (4/3\pi R^3)$

V = total volume of solution, or boundary velocity per unit total flux.

Z = number of ionized groups on macro-ion.

z = valency of ion.

α = number of effective charges of macro-ion ($= Z - \lambda$), or species of ion.

α' = degree of neutralization.

α'' = extended degree of neutralization.

β^{*}_{22} = rate of change of the activity coefficient of the polyelectrolyte component with its concentration.

δ = number of equivalent per gram of polymer.

γ_2 = activity coefficient of polyelectrolyte component.

γ_p, γ_g = ionic activity coefficient of macro-ion and gegen-ion.

δ_1 = mean radius of an ionized group (assumed to be a metallic sphere) and a gegen-ion, or distance between centres of dipole and adsorbed ion.

δ_2 = mean radius of positive and negative ions of salt.

ϵ = dielectric constant of solvent.

ζ = surface potential of charged particle.

η = viscosity coefficient of solvent.

κ = extended Debye's reciprocal length, or relative conductance.

κ' = original Debye's reciprocal length.

λ = number of counter-ions present in a macro-ion sphere.

μ_s = ionic strength of salt.

μ = moment strength.

ν_1 = number of ions of species i in a macro-ion sphere.

ρ = charge density.

ψ = electrostatic potential.

When necessary, some of the notations listed above were attached

subscripts, and superscripts,

p, s = polymer or salt.

i, j, α, β = species of ion.

Ds, As, del = descending, ascending, or delta boundary.

+, - = sign of charge.